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REFINER
AND NATURAL GASOLINE MANUFACTURER

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The Look Box

THE story of oil is still a success story. The industry continues to prosper and the prosperity promises to continue—at least for some months. The industry has been the first to reach the fabled corner where prosperity lies.

Success

Now rounding the corner at the highest rates of activity it has ever attained, the industry is challenging the record of earnings that it set in 1929.

If it does not falter or stumble in the remaining four months of the year, the oil industry will show for 1937 about 50 percent more profit than in 1936, and consequently about the same profit as in 1929.

The oil industry's markets continue generally firm, with prices mostly unchanged; as the outlook appears hopeful, while latest available statistics on operations are encouraging.

An improvement over last year is definitely revealed by reports on oil company earnings for the first six months of this year; and the third quarter is referred to as possibly the most profitable yet experienced. It would require unusual, unforeseen adversities in the closing months of the year to spoil the picture that is being painted.

While there has been some talk in recent months of a possible slowing down of business generally in the summer-fall period, the oil industry so far has not experienced any such letdown, and has shown no indication of any impending recession of real importance.

On the contrary, the Bureau of Mines expects crude oil and gasoline demand to continue showing about the same improvement over last year during September as in earlier months of this year. The Bureau's forecast indicates that in September the crude oil requirements should be 9 percent above requirements for September of last year and that gasoline demand should be up 10 percent. Such gains are about the same as for the earlier part of the year.

In as much as large demand means little in the absence of a proper balance of supply with the demand, attention still must center on regulation of the wells and the refineries of the country. In view of the anxiety that has attended the comparatively lax crude control during August, conservation officials have acted to tighten the restraints in September. This has helped restore steadiness in the industry's markets, and prices have been generally firm. This prospect of better balancing of production with demand naturally is encouraging and is reflected in the markets by increased confidence.

Meanwhile, the markets and the earning power of oil companies are supported by an advantageous inventory situation. Although petroleum demand has been running this year around 10 percent higher than last year, crude oil stocks are only slightly larger than at this time last year. Present gasoline stocks, too, are justified by market conditions. While the inventories are 11 percent larger than a year ago, the demand

also is running about that much higher. The increased demand for oils this year embraces higher consumption of most of the products of the industry. Record-breaking demand for gasoline reflects the fact that more automobiles are registered now than ever before and the further fact that the public has been more travel-minded during the current vacation season than for any year since the boom times of the 1920's. Other products that have been in wider use this year than last year include: kerosene, fuel oils, lubricants, asphalt and road oil. Fuel oil demand has shown an especially large gain, reflecting the continued increase of domestic oil burner installations, as well as further expansion of industrial activity.

Roads

HIGHWAY construction continues to present an ever widening market for petroleum road oils and asphalts. More than half of the roads in the state highway systems with a surfacing better than gravel or sand, are of the bituminous type, according to statistics of the United States Bureau of Roads. The designated rural primary state systems now include 340,160 miles, and at the beginning of 1937 the surfaced mileage was 289,103, or 85 percent, of which 113,695 miles were high-type surfaces and 175,408 low types. The mileage of the bituminous types on primary state roads at the end of 1936, including 6 varying types of surfaces was 128,975 miles.

During 1936 sales of road oil showed a gain of nearly 1,500,000 barrels or 21 percent over 1935, according to the Bureau of Mines. Increased construction of low-cost bituminous roads in many states is resulting in a growing demand for road oil and asphalt. According to the American Association of State Highway officials the bituminous road construction programs involving the use of road oil or asphalt totaled 13,393 miles last year. Mileage of bituminous roads completed during the year constituted 75 percent of all road construction of a type higher than gravel.

Increased activity in low-cost road building, along with revival of building construction and increased utilization in other fields, combined to 1936 an all time peak year in the consumption of asphalt. Total volume sold by refineries in this country last year amounted to 4,074,745 tons, up 35 percent from 1935 sales. The previous high was in 1929 when refineries sold 3,888,642 tons.

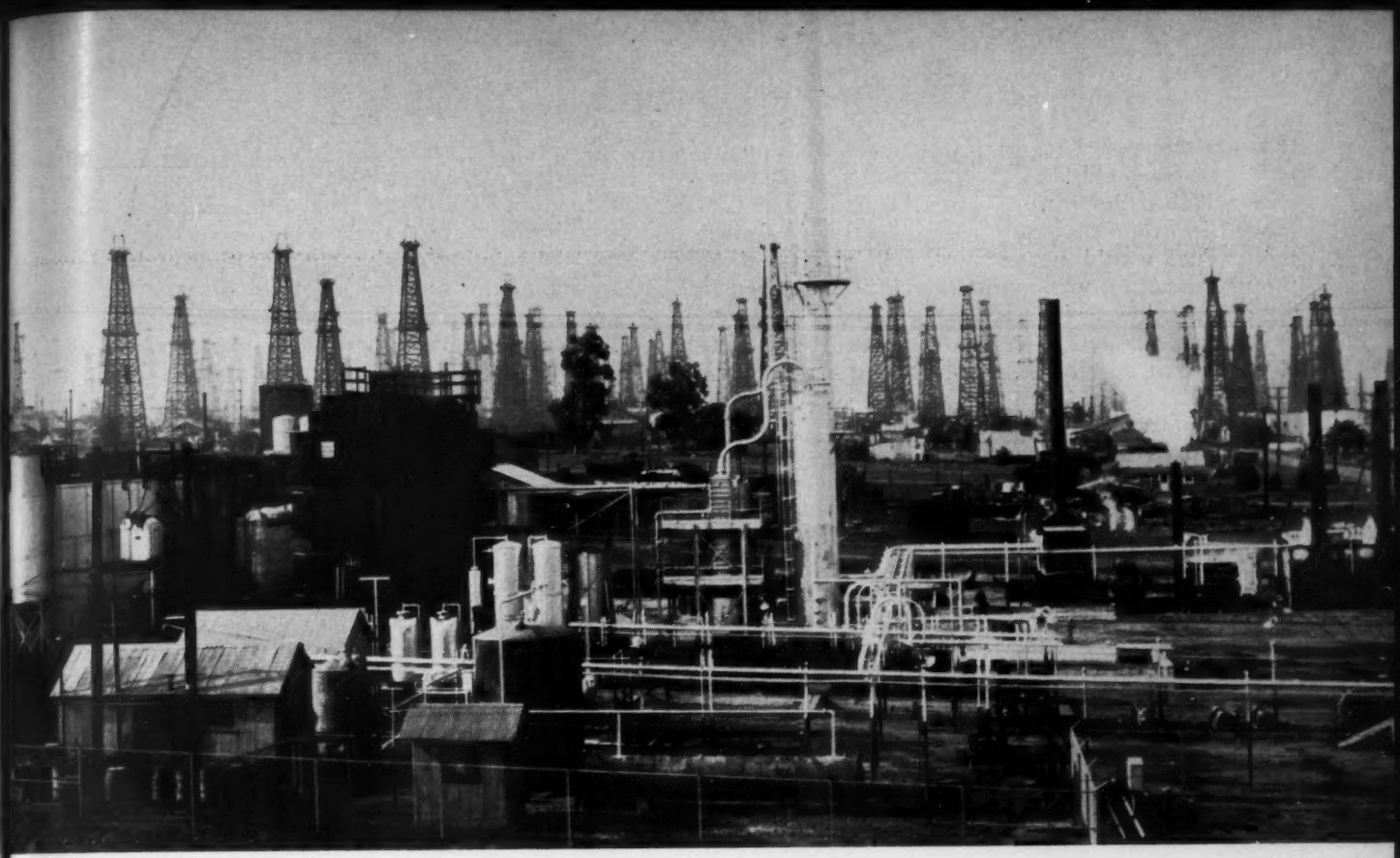
Of last year's asphalt tonnage, nearly three-fifths, or 2,365,926 tons, were used in road construction. This was an increase of 40 percent over sales of asphalt for paving in 1935.

Thus it appears that the organized and concerted efforts of the petroleum industry begun several years ago and directed toward the widening of sales of road oils and asphalts throughout the states has begun to pay dividends. But still more good business exists and only a portion of the available surfaces have been surfaced.

New Crude

THE crude oil produced from Ordovician lime, West Texas Permian basin in the Sand Hills field, western Crane County, is a wax-bearing paraffin-intermediate base oil having a gravity of 44.7° A.P.I., and a sulfur content of 0.22 percent, according to laboratory analysis made by the bureau of Mines, on a sample obtained from Gulf Production Corporation's Waddell 4. A distillation summary indicates approximately 35 percent of gasoline and naphtha, 20 percent of kerosene distillate and 25 percent of gas-oil and heavier distillate suitable for cracking. The crude is of greenish black color, with carbon residue of 1.3 percent with Saybolt Universal viscosity at 100°F. of 37 seconds. The naphtha fraction has a gravity of 66.1° A.P.I. and the kerosene fraction weighs 47.2° A.P.I. The residuum, 18.4 percent, has a gravity of 19.7° A.P.I. and a carbon residue of 6.8 percent. The analysis of this oil compares favorably with previous analysis on oil produced from the heavy-oil zone of the Ordovician strata in the Big Lake field, Reagan County, Texas. In separating the gas oil cracking stock fraction there is indicated 8.4 percent of 35.6 to 30.2° A.P.I. non-viscous lubricating oil distillate, and 3.9 percent of 30.2 to 28.0° A.P.I. gravity, medium lubricating distillate. No viscous lubricating distillate is reported.

Sand Hills is the second field to produce from the Ordovician strata in the West Texas Permian basin, the first being the Big Lake field. Gulf Production Corporation's Waddell 4 from which the sample was obtained, was completed at 6014 feet in dolomite, probably the Ellenburger formation. Although this was the third well to produce from this strata in the Sand Hills field, it is the first important well and produced by natural flow. The other wells are produced by pumping.



Design *of Bachmann Refinery Permits* Future Expansion

JOHN C. ALBRIGHT

BUILDING new refineries and moving old ones is sometimes a complicated process, influenced by local conditions which include labor, materials, source of crude supply and markets for finished products. When Bachmann Petroleum Corporation purchased a small skimming plant from Andrews Petroleum Company, Signal Hill, California, early in 1934, the officials of the company visualized the conditions surrounding the acquisition of the plant, and what effect closer spacing of wells in the Signal Hill field would have upon the operation of this refinery. In April, 1935, new producing wells caused considerable excitement in the Signal Hill field, with a possibility that the existing plant site would be covered by drilling equipment, which would not only hamper operations from a standpoint of sufficient space, but would create an additional fire hazard.

Due to these conditions and because of the necessity of increased output, a larger and more desirable plant site was selected upon which to locate the old equipment, and to add to the capacity by building additional facilities. The new location is situated on the north slope of Signal Hill which had both advantages and disadvantages, the first being characterized by the higher back of the plot, which made it possible to locate the crude supply tanks higher than the suction of the charging pumps. The disadvantage was that of the unequal drainage, causing soft spots in the soil, making it difficult to obtain stable footings for the columns and other heavy equipment.

CONTINUED OPERATION

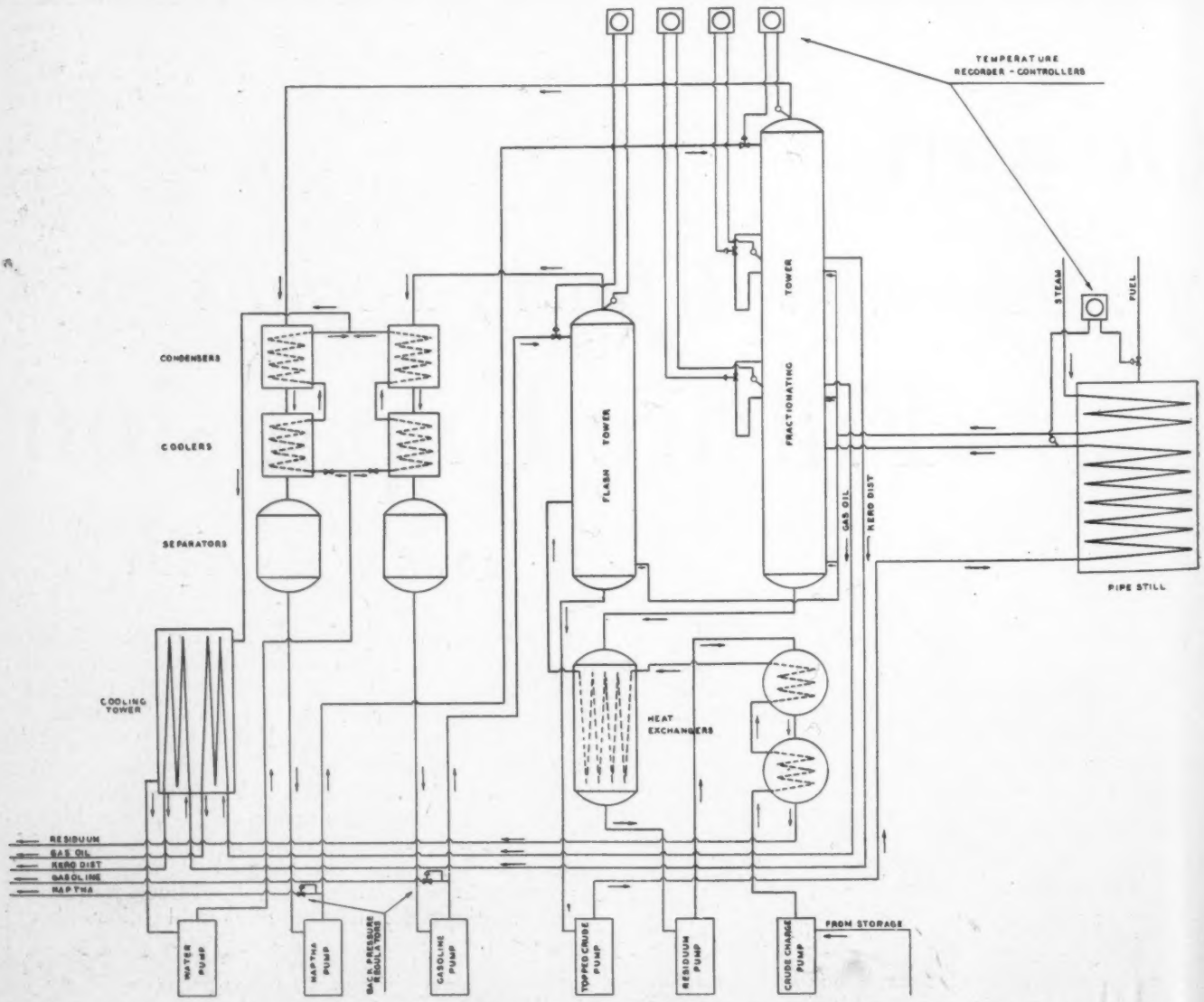
The plant continued operation while crude and finished gasoline lines were laid from the rundown

tanks to the new site, after which the treating plant was moved bodily. All connections were secured with which to hook up the treating unit after it was moved in order that only a small delay in finishing motor fuel would be encountered. The grading of the new location was made, foundations poured, and all other necessary arrangements made. Only one day was consumed in dismantling the treating unit, cleaning and moving it. Another day was necessary for connections to be made from the 3-inch gasoline line to the treating plant, and tankage. Two 5000-barrel bolted steel tanks had previously been erected on the sloping side of the new site. The site was graded in terraces to accommodate the variety of vessels required. While moving the treating plant, gasoline manufactured was pumped from the accumulator drums to one of the 5000-barrel tanks, which prevented a complete shut-down of refining operations. As soon as the treating plant was again placed in operating condition, the stored raw gasoline was pumped through the treater.

Preparations were being pushed rapidly for a complete removal of the older plant when certain conditions made it apparent that drilling would not be pushed rapidly on the old plant site, which fortunately made it possible for the engineering staff of Bachmann Petroleum Corporation to make a more extensive survey of their requirements. Most of the standard refining equipment was thoroughly investigated to determine which type of pipe still, fractionating columns and pumps would serve better when erected on the new plant grounds.

While small, the new location of about 5 acres could be laid out to accommodate the required amount of refining equipment and leave sufficient space for a projected cracking unit. With future expansion always in view, the property was laid out upon the drafting table, so that all equipment needed would occupy as small a space as practicable, yet not crowd the units unduly. Consequently, during the few months occupied by the "breathing spell," the plant was operated from two different points, separated by about ¾ mile, with the distillation being carried on at the old plant, while crude storage and gasoline treating were handled at the new site.

Practically all of the different parts of the new plant are new and modern in design and efficiency. The flow sheet of the projected plant called for a



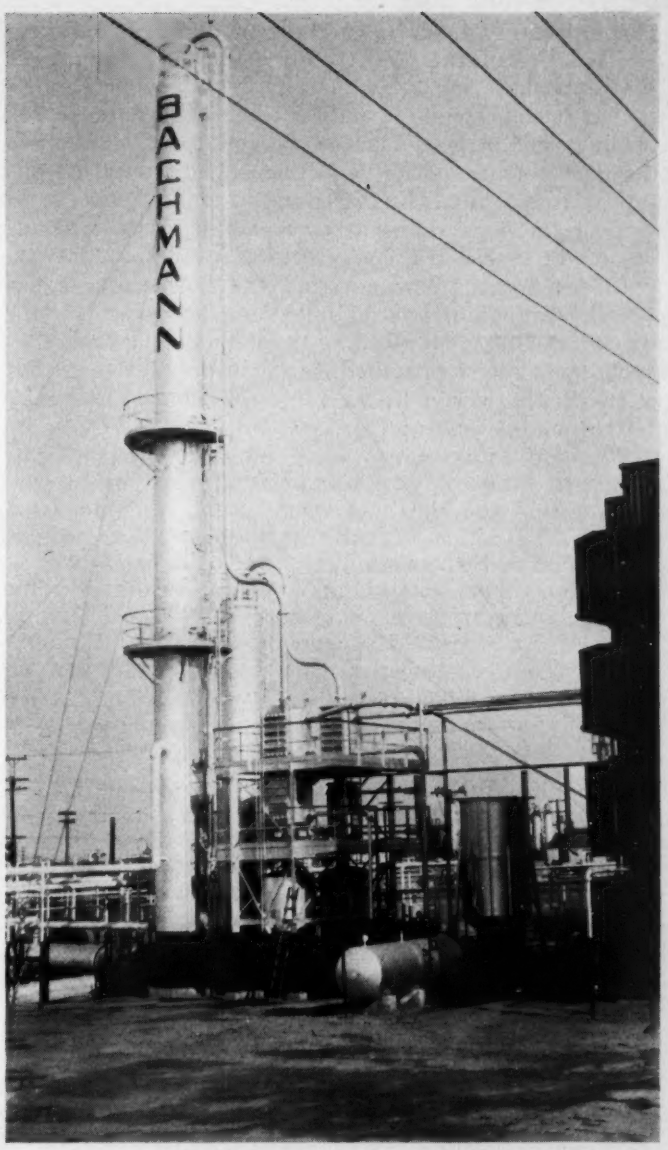
Flow diagram of distillation unit. Bachmann Petroleum Corporation, Signal Hill, California.

conventional double flashing of the crude, with extra provisions for separation of the two streams of gasoline from the top of the towers, to prevent contamination of either. The main column is 90 feet in height, used to remove a naphtha cut as an overhead stream and two side cuts; kerosene distillate and gas oil. The primary column is 34 feet in height, designed to remove only the more volatile fractions, constituting a high gravity straight-run gasoline.

LEISURELY CONSTRUCTION

Construction was carried on in a somewhat leisurely manner, using only a small construction crew, while most of the preliminary work was being accomplished, such as grading for new tankage, making dikes for fire protection and making the new plot into condition to receive the major units. When purchasing had been completed, and delivery assured, the crew was enlarged sufficiently that most of the foundations and concrete retaining walls could be poured rapidly. With this detail cared for, erection of equipment was easily done as soon as it arrived in Signal Hill. The separate units, such as flash and fractionating columns, condensers and coolers, heat exchangers and the like, were placed as closely to each other as operating conditions would permit, yet not so one would interfere with the other.

Crude is received by pipe line and by truck, both supplies being placed in one of the two 16,000-barrel, all steel, welded tanks from which it is pumped



Main and flash column in Bachmann Petroleum Corporation's plant at Signal Hill. Photograph shows that vapor lines from these columns are attached to separate condensers to prevent contamination of streams.

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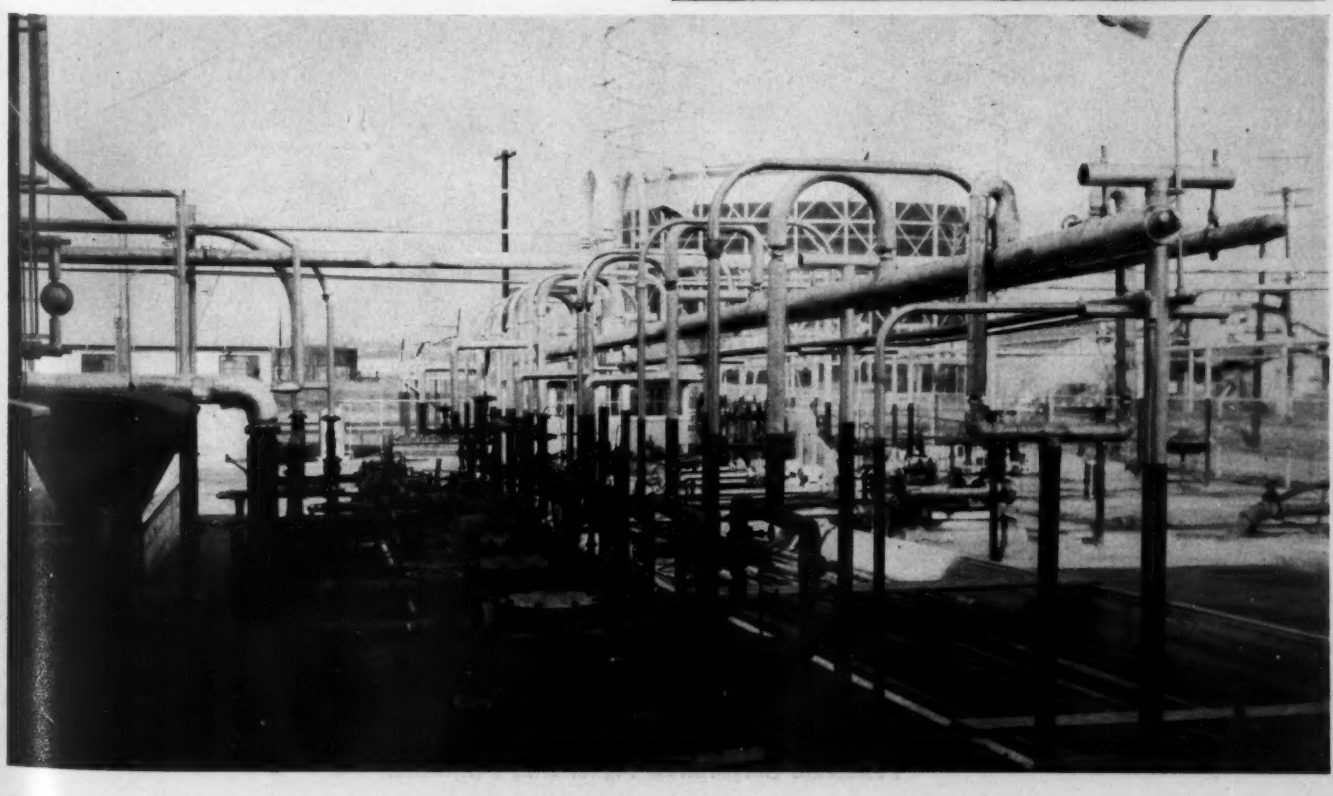
Both live and exhaust steam lines are carried on overhead stanchions, utilizing pipe bends to prevent back pressure on the exhaust and to obtain maximum pressure from live steam.



through exchangers (residuum to charge), entering the smaller of the two columns for exchanger heat distillation.

Concrete was poured outside the refinery fence for loading refined products and for unloading crude oil, the trucks being driven upon them, which prevents unsightly ruts around the place, and to make it more convenient for maintaining a clean pair of racks. Unloading of the trucks is accomplished altogether by gravity, with the liquids flowing from the truck and trailer vessels through the usual unloading hose, which may be connected to pipes leading to underground vats. Two receptacles were provided for such unloading, so that if two trucks arrive at the same time, both loads may be inspected separately.

The unloading sumps were built in the northeast corner of the yard, as close to the property line as possible, where the slop and waste water skimming vats were built. Pumps located near these vats are used to remove oil and water, the first, after being made free of all excess water, being pumped to the wet oil tanks for subsequent treating in an electric dehydrator. Dry oil received from trucks, showing the minimum amount of b s & w is pumped directly to the crude working tankage. Wet oil received, also from trucks, is treated in the same manner as salvaged oils from the waste water skimmers.

BOILERS

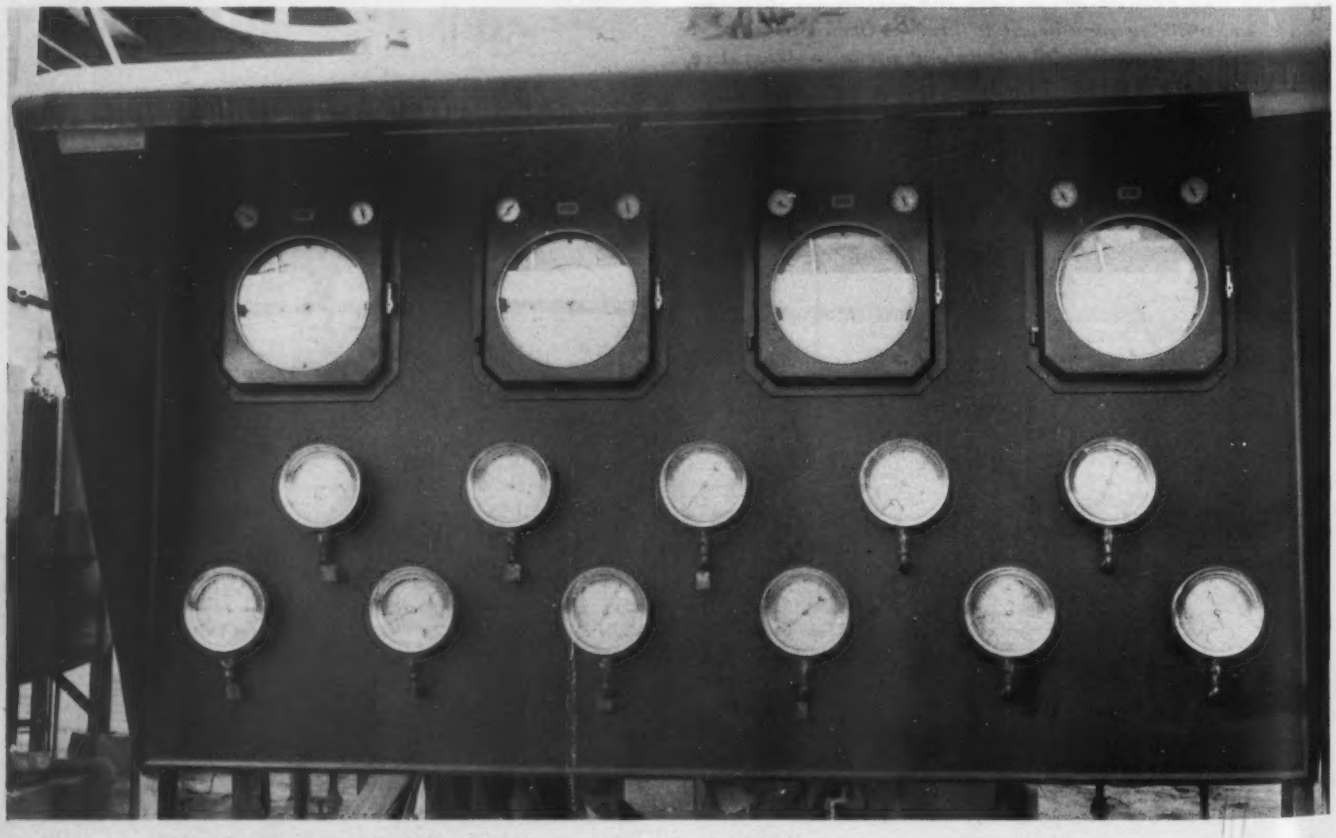
Boilers used in the old plant could not be moved while refining was being done at that location, neither could immediate working tankage or other accessories. New equipment, so far as practicable (taking into consideration the salvage value, as well as the utilitarian value of the old plant) was installed throughout the new plant. When it had been brought to a point where it could be fired, the old plant was shut down and transfer of materials begun. Fires were pulled in the boilers and still on August 11, 1936, which provided about 18 days between drawing the fires in the old plant and firing up the new one. During the interval, five 2000-barrel steel tanks were dismantled and moved to the new plant where they were erected on the terrace above the distillation equipment.

All of the pumps which had not seen an excessive amount of service, and which could easily be repaired, were overhauled and moved. Those condensers and coolers that could be used again were overhauled, taken apart and retubed while the interior of the tube covers (which were square shell and tube units) and the tube sheets were sand blasted and sprayed with metal to prevent corrosion from water or oil. Fifteen actual working days were consumed in moving the used equipment and making the necessary connections in the new plant. While 18 days elapsed during the shutdown, Sundays were not included, as no work was done on these days.

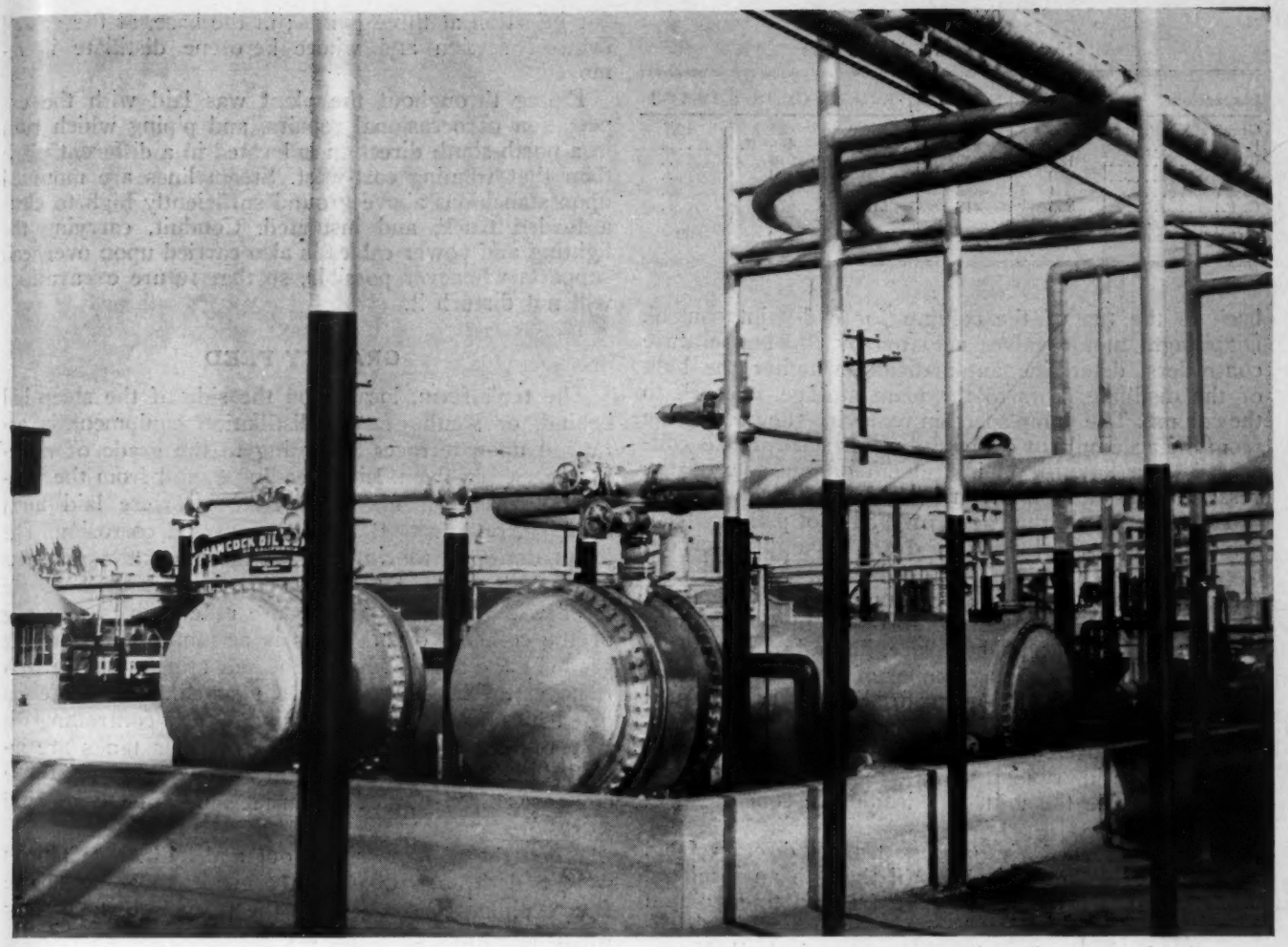
On August 29 the pumps were started with water to wash out all lines and to make sure no leaks were in the connections. Oil circulation was established about 12 o'clock, fires were started in the still, and by late afternoon, equilibrium had been reached in the columns and refining of the crude was under way. No insulation had yet been applied to the exterior of the columns or exchangers, which caused some lag in arriving at the proper balance between charge, stream and reflux. Specification products were being removed from the accumulator drums the first day.

PUMPS GROUPED FOR CONVENIENCE

All of the pumps were arranged so they would face the control panel, containing the recording controlling



Control board with protecting steel roof extending over instruments, Bachmann Petroleum Corporation, Signal Hill, California.



Battery of heat exchangers protected by retaining wall.

instruments, so each unit could be easily watched and maintained by the stillman on duty, without taking too many unnecessary steps. Maximum production is what Bachmann Petroleum Corporation desired when the new plant was designed and built, and with all units grouped for convenience in operating this can be obtained easly; much more so than if pumps were set in groups of two or three, and scattered at various points in the yard. Efficient operation was built into the plant by using as many as necessary of the standard automatic regulators and controllers.

The pumps, most all of which are reciprocating, steam-driven units, are mounted upon concrete foundations, well spaced and high enough from the grade level to allow operation and maintenance to be easily carried on. Each pump, being matched with a spare for an emergency, is mounted upon steel framework between its base and the concrete foundation to eliminate the need of grouting the base to the setting. This practice, it is said, also provides for greater ease when removing one pump to be replaced with another if repairs are required that cannot be made while it is on the foundation. Some of the pumping units are electric motor-driven, and those that are powered by this type of prime mover include the water circulating pump, lubricating oil circulating pump and the caustic solution to vapor line pump.

The pump for charging from the crude oil storage tank, located on the highest terrace above the distillation unit, picks up the oil and moves it, first, through two conventional shell and tube exchangers and, second, through a large, longitudinal vessel, filled with tubes and baffled. Both these sets of exchangers were installed to obtain sufficient heating of the crude charge that a considerable amount of the lighter fractions might be removed before the bulk of the charge entered the pipe still. After leaving the exchangers (countercurrent flow of hot, stripped residuum passing through the units from the base of the main column) the crude enters the shorter of the two fractionating columns. Two cuts are taken from this column, overhead being gasoline having a gravity of about 64° A.P.I. and topped crude.

OPERATION

Topped crude is pumped from the base of the column by one of the reciprocating pumps controlled in speed by a liquid-level controller mounted upon the side of the column so that topped crude is removed as fast as fresh crude is pumped into the column. The stream of gasoline vapors taken from the connection on top of the column passes through two sets of water serviced coolers, the first above the second, both mounted upon a steel framework. This stream of gasoline is received in its individual accumulator drum and water separator, set directly below the pair of condensers from which a steam-driven pump takes suction, delivering the condensate from the receiver to the storage tanks on the terrace. Automatic temperature controllers on the instrument panel regulate the amount of reflux delivered

TABLE 1

Specifications of Products

Inspection	Gasoline	Naphtha	K. D.	Gas Oil	Fuel Oil
Gravity, ° A.P.I....	64.0	47.0	37.0	34.0	16.7
I. B. P.....	85° F.	218° F.	438° F.	488° F.	.....
10% over.....	138	262	456	514	.....
50% over.....	250	323	468	546	.....
90% over.....	304	396	492	628	.....
E. P.....	365	418	518	674	.....
Flash, Pensky-Martin closed cup...	.....	.....	200	230	320

back to the top of the column for end-point control. Diaphragm motor valves actuated by the temperature controllers, determine automatically whether the bulk of the distillate flows to the plant storage, or back to the column. The pump speed in removing the condensate from the accumulator drum and water separator, is controlled by a liquid-level instrument on the side of the vessel to maintain a predetermined level therein.

Topped crude in the base of the 34-foot primary flash column is removed by a topped crude pump which delivers it directly to the pipe still. The pipe still is a refractory lined steel box. Self-suporting, light weight, low carbon steel tubes were installed in the furnace with return bends welded in place, instead of removable headers. The combustion chamber of the still was made on the type of a Dutch oven, fired with gas, designed so the flame travel is below the bank of tubes. Automatic temperature control is maintained upon the transfer line by an instrument mounted upon a small control panel set beside the unit, and inside the concrete firewall.

The topped crude in process travels directly from the transfer line of the pipe still through an insulated line to the side of the 90-foot fractionating column where it is separated into four products: naphtha, kerosene distillate, gas-oil and residuum, or fuel oil. Naphtha, having an A.P.I. gravity of about 47° is taken from the top of the column. The uncondensed vapors are contacted in the vapor line, with a solution of caustic soda to counteract what hydrogen sulfide may be evolved from the sulfur in the crude when heated to processing temperature. Liquefied and cooled naphtha is pumped to proper storage, with a part of the stream being returned to the top of the column for qualitative control. Automatic controllers were installed at essential points to maintain the desired temperatures in the unit, similar to those on the first column and its complement of pumps.

Kerosene distillate and gas-oil are both removed from the side of the 90-foot column, recorder-controller instruments operating valves in the "bootlegs" on the side of the column for self-refluxing, make unnecessary the operation of pumps, as the height of the draw-off pans provide sufficient head to permit the liquids to flow by gravity through the coolers to storage. Atmospheric cooling sections were installed in the water basin of the cooling tower to reduce the temperature of both these cuts so storing may be done without loss from excessive evaporation.

Steam for power and processing is generated in three 70 horsepower H.R.T. boilers, fired with gas and equipped with automatic fuel controllers to maintain the required pressure. Part of the steam from the boilers is taken from the overhead header and led to the pipe still, which is equipped with a bank of superheater coils, to dry out the steam before it enters the columns in the distillation equipment. The 34-foot column receives steam at the base, while the 90-foot vessel is equipped for injection at three points; in the base, at the gas-oil drawoff section and where kerosene distillate is removed.

Piping throughout the plant was laid with the expectation of occasional repairs, and piping which runs in a north-south direction is located in a different plane than that running east-west. Steam lines are mounted upon stanchions above ground sufficiently high to clear a loaded truck, and insulated. Conduit, carrying the lighting and power cables is also carried upon overhead supports whenever possible, so that future excavations will not disturb it.

GRAVITY FEED

The tank farm, located on the side of the steep hill behind, or south of, the distillation equipment is arranged upon terraces according to the grade of material carried in them. Lines leading to and from the various vessels built upon the terraces, were laid upon blocking, or low trestles to prevent soil corrosion. The tanks designed to contain the more volatile products were equipped with water seal tops, and all tanks are fitted with vacuum and pressure relief valves. Gauging of the contents of all tanks is accomplished from the grade by the use of vapor-tight indicating gauges, which removes the necessity of the gauger climbing to the top of each tank several times daily. Valves controlling the flow of liquids to and from the various tanks are installed at a convenient height, above ground, so the operator is relieved of a considerable amount of hard work.

When the plant was laid out and built, pipe nipples were laid through dikes and firewalls to accommodate future piping to serve when the plant is expanded, or when additional facilities are provided, such as cracking. Sufficient space for a plant of this type was left vacant just west of the crude distillation unit, and south of the pipe still.

Shipping of all products, with the exception of residuum, or fuel oil, is done largely with truck and trailer units, which load at the refinery entrance under one of the loading racks built when moving of the refinery was first begun. Residuum is handled by a pipe line, which delivers the heavy oil to gathering lines maintained throughout the Los Angeles Basin, leading to refineries operated by the major oil companies. A large, high-pressure, steam-driven reciprocating pump is used to handle the cooled residuum, and pumping is done when dispatchers of the lines clear them for use. Loading of the truck and trailer units is accomplished by electric motor-driven pumps, located in the building at the plant entrance, operated by push-button control, with the products measured by positive displacement meters.

The automatic features of the plant are of such character that when the plant has been placed on stream, and equilibrium obtained within the columns, one operator is all that is required with each shift. Extra operators, or yard men are in the plant during the day to make what repairs are necessary, and at night, an extra man performs the duties of laboratory inspector, loader and receiver of crude.

The writer wishes to express his appreciation for the helpful assistance of Charles S. Cox, refinery superintendent, who so graciously gave of his time during the Christmas holiday period, to place the foregoing information at his disposal.

Special Columns Yield Wide Variety of Products at

Barnsdall's Earlsboro Plant

BARNSDALL OIL COMPANY had been operating a gasoline plant in the Earlsboro field, near Seminole, Oklahoma, for a number of years, manufacturing the usual grades of natural gasoline in a more or less conventional manner by utilizing the absorption system, until early summer in 1936, when it installed a battery of four fractionating columns in order to manufacture special products.

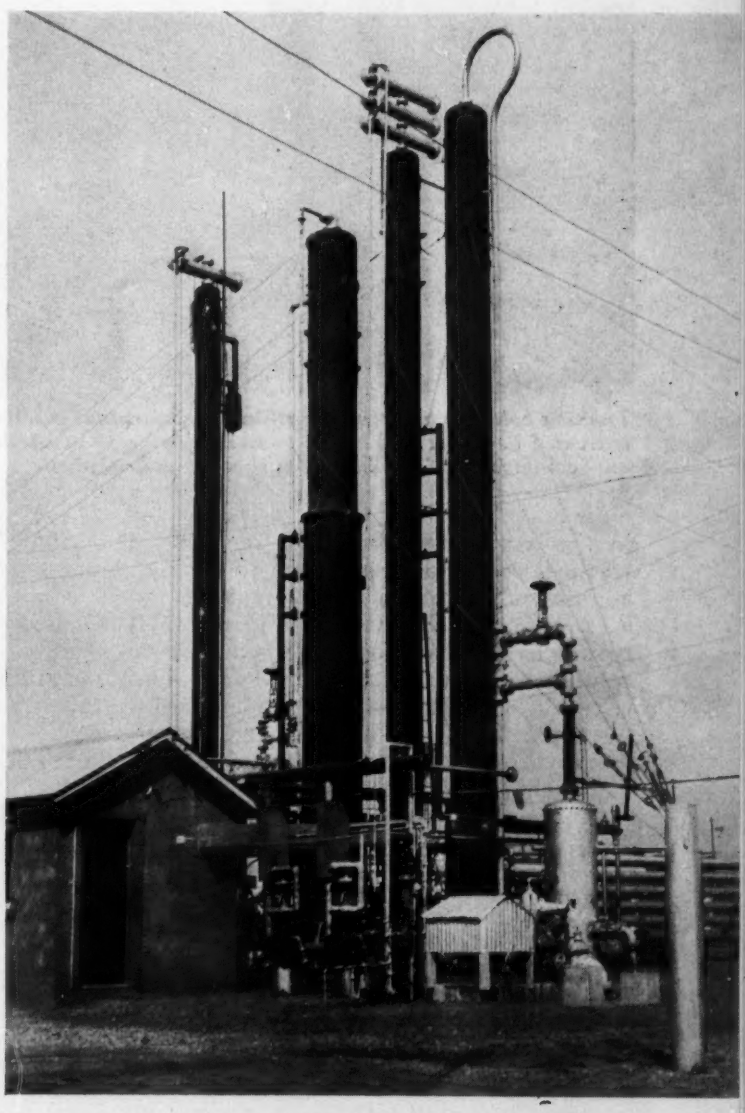
Prior to this time, special products, such as propane and butane, were not considered by a large number of gasoline manufacturers as fractions that had a definite value except on a limited market. Gasoline graded as 26/70, or lower vapor pressure, compelled these plants to stabilize their production by eliminating propane and a certain amount of butane so their product would meet market specifications. During the past two years, thermal polymerization has received considerable impetus, which has created a wider demand for special fractions, and improved methods and facilities for distribution has created a definite demand for both propane and butane for use in communities where natural gas has not been available.

Mixtures of propane and butane, varying in percentages, are being demanded by motor transport companies in some sections of the country to supplant ordinary motor fuel for use in heavy-duty engines, as are drilling contractors where natural gas or fuel oil is not readily obtainable. Some contractors prefer butane, as the mixture is called, to either gas or fuel oil, as costs of using it compare favorably with other fuels, and some operators prefer it because of its superior power-generating qualities when compared to Diesel and fuel oil.

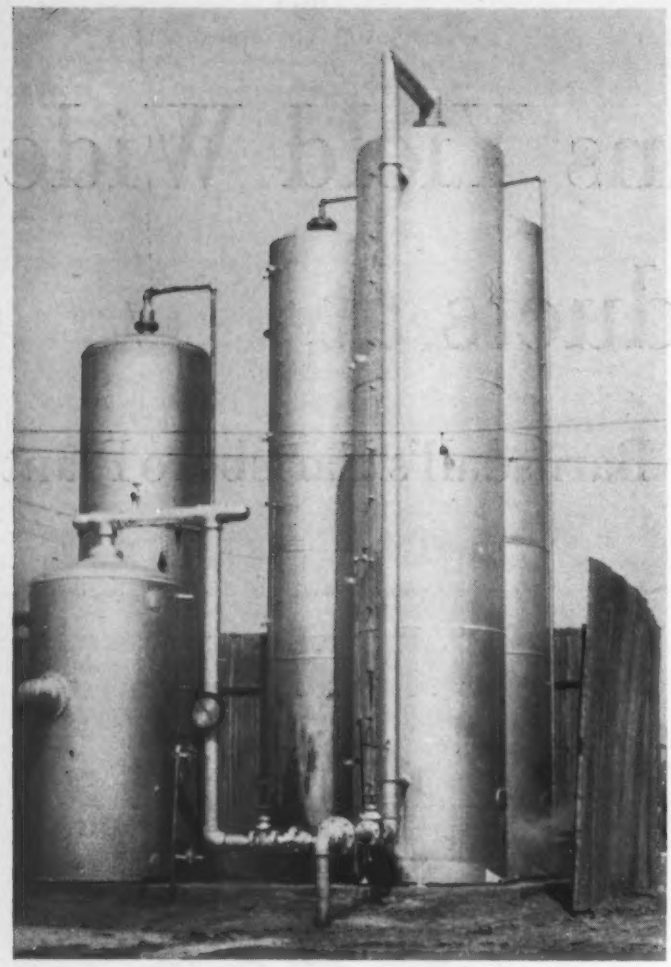
In order that the company might be able to take advantage of markets available for propane and butane, as well as markets for other liquefied petroleum gases, such as rubber solvents, paint and varnish thinners, pure propane, pure butane and pentane and hexane, a battery of special fractionating columns was installed in its plant near Earlsboro. Four columns were included to process the usual production of raw, unstabilized natural gasoline made in the absorption plant.

The columns are all of the 30-plate type, ranging from 16 to 30 inches in diameter, each equipped with reboilers, reflux pumps, or reflux condensers placed on top, control instruments to insure definite flows of liquids, gases and cooling waters, through the various parts, and to regulate the amount of heat supplied by steam to the reboilers and pre-heaters.

The production of absorption gasoline is handled



Special products columns used by Barnsdall in its Earlsboro gasoline plant to manufacture any grade of natural gasoline, propane, butane, pentane and hexane from gross production of absorption plant.



Treating columns and tanks in which all absorption gasoline is treated before it is pumped to working storage at special columns in Barnsdall's Earlsboro gasoline plant.

in the usual manner in the recovery plant, but is washed with caustic solution to remove what small amount of hydrogen sulfide may be in the condensate. Immediately after this pre-wash, the gasoline passes over into a conventional vertical contacting column where calcium hypochlorite is used. Gasoline rises through the treating liquid and is taken off overhead in the usual manner. After treating, it passes through a vertical settler so that no foreign material will be in the gasoline.

Vapors from the accumulator tank and the stock tanks are returned to the engine room where one of the compressors converts the propane and other fractions with a higher boiling range than ethane into liquids by compression and cooling. This product is blended with the absorption gasoline in a constant proportion so the blend will possess a consistent gravity and vapor pressure, A long, horizontal, comparatively small diameter tank is used to receive this blend, and acts as a supply tank for the special column plant. To insure adequate mixing of the compression gasoline with the absorption production, both liquids, in a state of blending, are admitted to one end of the tank, opposite from that from which they are removed for final processing.

Pressure of about 275 pounds is maintained on this blending and special column supply tank to prevent the escape of any fraction in the liquid contents. The gasoline having a vapor pressure of about 36 pounds, Reid, is withdrawn by a steam driven close clearance piston pump, 8x4x12 inches and delivered to the first, or depropanizing column under a pressure of 300 pounds, gauge. This raw charge, including all the propane that it is possible to extract from the gas passed through the recovery system, flows through a conventional heat exchanger against the bottoms from the depropanizing column so that the depropanized product is cooled, and the charge is heated. Several entrance nozzles are placed in the first special column for proper temperature delivery to the tower in order that fractionation may be obtained readily.

INSTRUMENT CONTROL

This column is equipped with five control instruments mounted on the control panel in the control house. The top of the tower is operated at a temperature of 122°F. by returning sufficient of the overhead condensate to obtain this condition. One of the instruments regulates the amount of the liquid reflux so the vapors taken from the top connection will be commercially pure propane. This instrument also controls the pump discharge so that liquids not required for column control will pass directly to the de-ethanizing and de-hydrating column for a final processing of the propane fraction removed from the charge. A similar instrument connected to adequate valves controls the volume of steam passing through the reboiler so that a temperature of 280°F. is maintained on the liquids in the base of the tower. Charge to the column is fixed definitely by a flow controller attached to the steam line leading to the charge pump in order that the flow of raw gasoline will be constant at all times, which prevents "rocking" of the temperatures. Pressure is maintained at 300 pounds gauge, by one instrument so that fractionation will not fluctuate and cause off-specification production at the vapor outlet or that remaining in the base of the column.

Bottoms from this column travel directly to the next in line under system pressure and are propane-free liquids. The de-propanized material flows through a second bank of heat exchangers placed on the outlet of the second column so that a proper heat balance will be obtained. Three recording-controlling instruments are used on this column, one of which maintains an overhead temperature of 118°F. by regulating the volume of water flowing through the overhead reflux condenser. A similar instrument controls the amount of heat needed in the reboiler by allowing a definite amount of steam to enter the tubes so that 240°F. will be transmitted to the material in the base of the column. A pressure of 80 pounds, gauge, is carried on the column at all times when making a butane-free gasoline, and is accomplished by the third instrument connected to this column.

MAKING SPECIAL PRODUCTS

The results obtained in the third column depends entirely upon the material desired as a finished product. If special products are to be manufactured, such as pentanes, in the overhead vapor stream, and hexane and heavier is accumulated and withdrawn from the base of the column, butane free gasoline from the second column is fed to the third for this purpose. However, if a 26/70 natural gasoline is required, the gasoline is debutanized in the second column to an extent that it will furnish a finished

gasoline without passing through the third tower. However, the function of the third column is to provide a finished product, overhead, which may be either pentane or hexane, depending upon the method of operation and the composition of the feed.

Pumping is necessary when operating this column due to the fact that the de-butanized material from the second column is always run to working storage rather than directly to the third column. This was the method designed because any number of special products may be required so that a more or less batch operation is followed. For example, when pentane is the chief overhead product, or this fraction is to be manufactured so the boiling ranges fall between 85° and 100°F., the column has an operating pressure of 30 pounds. This pressure is maintained by one of the 5 special instruments connected to the tower. An overhead temperature of 155° F. is carried. Overhead, pentane in this operation, is condensed in sections placed near the column, and a portion is pumped back to the top of the column for overhead temperature control. One of the instruments on the control panel regulates the volume of liquid, and also permits excess to flow to storage. The reboiler temperature is maintained at 251°F. in the usual method of controlling the amount of steam necessary to the reboiler.

A variety of products or special cuts may be prepared with this column. By varying the composition of the feed to the column, pentane may be the overhead production, but with this fraction removed, the next lower-boiling hydrocarbon may be recovered. If a straight-line flow is desired, and propane, butane and pentane are required, the material passes from one column to the next as rapidly as conditions will permit. Batch operation is resorted to only when special products are desired which require reprocessing when exceptionally close-boiling materials are needed, or, the inclusion of several fractions in one liquefied product.

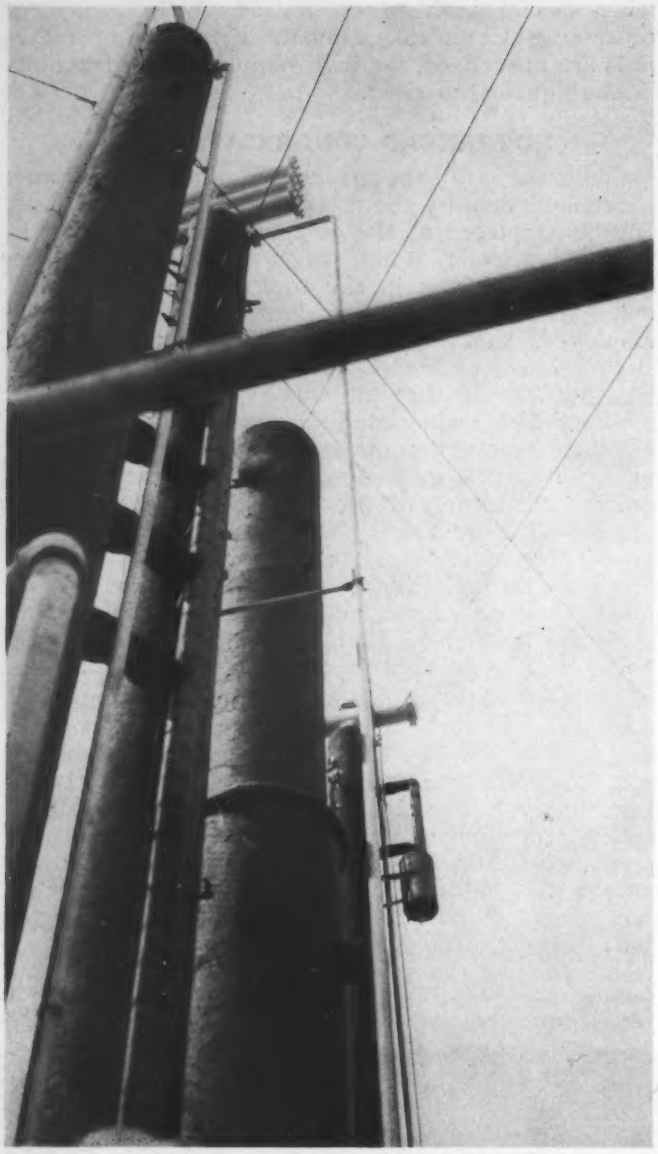
OVERHEAD CONDENSATION

Condensation of the overhead production, propane, is accomplished by the use of two separate sections, one being placed at the column, and the second in the cooling tower. When atmospheric conditions permit, the condenser in the tower is by-passed, but when warm weather is encountered, both units are employed. Complete liquification of the overhead stream is maintained, and the temperature is lowered sufficiently that the vapor pressure is reduced to that which makes handling more economical.

When market requirements are such that any grade of natural gasoline is to be manufactured, operating conditions of the debutanizing column are applied which makes it possible for an 18, a 20, a 22 or a grade of 26/70 to be manufactured with only one pass through the column. In this case, the required amount of the butanes are extracted as an overhead fraction so that the bottoms from the reboiler will be finished gasoline.

Propane taken from the first tower is pumped by the reflux pump to the de-ethanizing column, which also removes all moisture from the liquefied gas. Overhead from this column is led to the boiler fuel-supply line and burned for the production of steam. An overhead, water-cooled unit holds the desired temperature on the column top so that all the ethane and lighter will escape, but all the propane will return through the fractionating plates to the base for withdrawal as finished liquid. A side-pot is attached to the column near the top to accumu-

Control panel in Barnsdall's Earlsboro gasoline plant, showing instruments used with special columns for manufacturing various close cut products from natural gasoline.



Looking upward at special columns in Barnsdall's Earlsboro gasoline plant which was remodeled recently so special products may be manufactured from natural gasoline. First Column: depropanizer; second column: debutanizer; third column: special products, such as pentane and hexane, and fourth column used to de-hydrate and de-ethanize propane before shipping to storage or tank cars. Pot on side of last column is water accumulator.

late condensed moisture and so it may be easily disposed of without passing out with the fractionated propane.

If and when propane is not required as a separate product, the condensate from the top of the first, or de-propanizing column, after serving the purpose of reflux, is revaporized and led to the fuel lines of the boilers for fuel, the same as is ethane from the final column in the system. It is not fed back into the lines leading to the gas engines driving the compressors because of its high B.t.u. content, which would act unfavorably upon the power cylinders if taken into the mixers in excessive quantities.

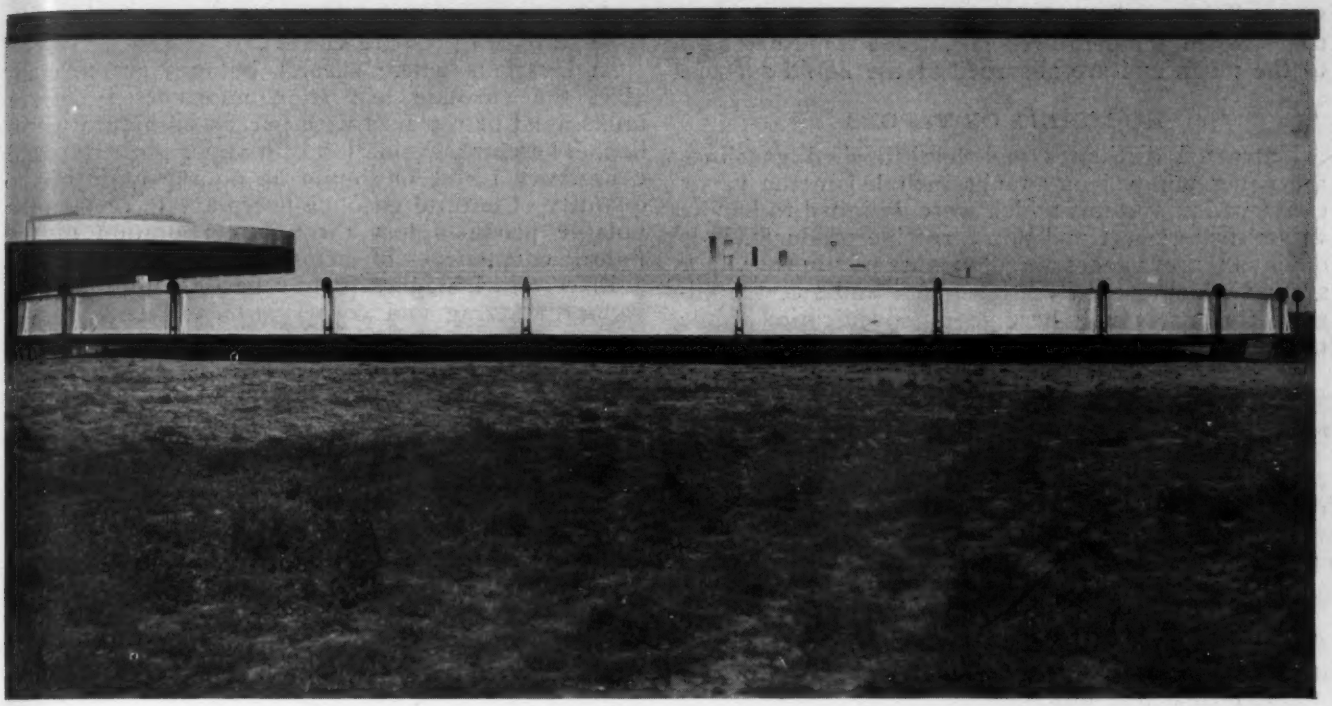
Four tanks are installed at the special column part of the plant so that special cuts may be run to them when extra processing is required. Any special product, such as commercially-pure propane, butane, pentane or hexane, as well as the regular natural gasoline grades, is pumped to individual tanks prior to loading out for transportation. The greater portion of the special cuts are shipped in tank cars loaded on a rack about a mile south of the plant.

SPECIAL COLUMNS SEPARATE UNIT

Operation of the special columns is facilitated by the primary manufacture of a constant gravity and vapor-pressure absorption and recompressor gasoline. By having a constant composition feed, fluctuation of the operation of the special columns is presented, and supervision is reduced to a degree not obtainable when a varying feed is pumped to the fractionators. The special columns are in an independent unit, dependent only upon natural gasoline for operation, containing its individual water system and pumps for circulation. Power for the single electric-driven centrifugal water pump is received from the auxiliary room of the absorption plant, and steam received from the common boiler plant. Air to operate the motor valves of the instruments which control the operating conditions of the plant is compressed at two points, one in the boiler room by a locomotive-type compressor, and in the auxiliary room by a gas engine-driven compressor.

The operation of the Earlsboro absorption plant was not disturbed by the erection of the special columns, and the only change necessary was that of obtaining a larger circulation of mineral seal oil so that all of the lower-boiling fractions in the gas could be absorbed and recovered for processing. Partial stabilization by selective absorption was accomplished prior to the addition to the plant so that the rich oil would not carry such a great percentage of the lighter fractions, which previously were not desired.

The propane recovered can be made with a tolerance of 2 percent, as can the butane. Pentane falls within the boiling limits of 85° F., I.B.P., and 100°F., E.P. Hexane is made with an initial boiling point of 144°F., and an end point of 158°F. Heptane, when manufactured from the bottoms from the special products column, has an initial boiling point of 194° F., and an end point of 212°F.



Steel Balloons and Vapor Gathering Systems Reduce Evaporation Losses

CHARLES D. HULL
Continental Oil Company

SINCE refiners generally have become evaporation loss conscious, greater efforts have been expended to conserve desirable fractions contained in freshly produced crude oil, and raw and unfinished refinery products which, because of their composition, will evolve vapors that will breathe from ordinary storage vessels, outward while temperatures are rising and inward as the contents become cooled. Losses have been checked when breathed from unprotected tanks that run into thousands of gallons annually, while contamination of the contents, due to breathing inward of dust particles, has caused gasolines to become off-color in some instances.

Conservation of light petroleum products, by the reduction of losses from storage vessels, has been accomplished by the application of the balloon principle in closed vapor systems at several of Continental Oil Company's refineries. The first installation of the breather balloon system was made in the latter part of 1934 at Ponca City, Oklahoma, followed immediately by similar equipment at the refineries at Wichita Falls, Texas, and Glenrock, Wyoming. The most recent installation of this type of vapor conservation system was made in the refinery at Denver, Colorado.

Calculated on the basis of full inflation, the balloon system at Ponca City has a capacity of 350,000 cubic feet, those at the Wichita Falls and Glenrock refineries have 150,000 cubic feet each, and the one at Denver has a capacity of 100,000 cubic feet. The system was installed in Ponca City and attached to one 25,000, three 80,000, and three 66,000 barrel gasoline storage tanks. Glenrock system serves 15 tanks, ranging from 500 to 55,000 barrel capacity, and the installation at Wichita Falls is connected to 21 tanks, having capacities of from 500 to 55,000 barrels. All of the vapor conservation systems were tied into the storage vessels by using light sheet metal piping 11½ inches in diameter. Gauging of the contents of these vessels is through special hatches which prevent the outflow of vapors. In addition to being connected to storage tanks containing finished and semi-finished gasoline, some of the systems are extended to include agitators and rundown vessels.

The purpose of the balloon system is to provide temporary storage for the vapors breathed from the tankage, which if permitted to escape to the atmosphere would be lost beyond recovery. When atmospheric temperatures rise during the day, gasoline vapors are formed in the storage tanks at the liquid surface which expand and are forced through the

vapor lines to the balloon. At night, and at other times when temperatures fall, these vapors return to the tanks and are absorbed at the liquid surface.

NO MIXING OF VAPORS

Untreated distillates and semi-finished gasolines are never pumped into tanks included in the vapor conservation systems which were designed to handle vapors from sweet and non-corrosive products. It is obvious that if vapors are allowed to mix in the vapor system which come from both sour and sweet products, the sweet will become off-specification while the sour products will not be affected.

In considering the economics of a gasoline conservation system, one must recognize three major sources of gasoline storage losses, which are:

1. Pumpings to and from intermediate and finished gasoline storage tanks, losses from which are caused by:
   (a) Pipe line leakage.
   (b) Vapor emanation due to exhaling tankage into which gasoline is pumped.
2. Pumpings from finished storage to tank cars, tank trucks and steamships, losses from which are caused by:
   (a) Pipe line leakage.
   (b) Vapor emanation due to exhaling tank cars, tank trucks and steamships into which gasoline is pumped.
3. Tank breathing causing the transformation of liquid to vapors, their escape through leaky roof seams, gauge hatches and other connections which are not both liquid and vapor tight.

The installation of a vapor gathering and conservation system tied into a flexible steel balloon will not eliminate all losses shown above, but certainly if the system is kept free of leaks, and operating satisfactorily otherwise, it will eliminate those resulting from tank breathing and emanation of vapors during the filling period. Such a system, however, will not eliminate pipe line leakage (which in any refinery is no small amount) but will lead to locating line leaks, because it definitely eliminates evaporation losses from the tanks to which it is connected; and if the storage loss figures too high after a reasonable time, one must definitely conclude that there is line leakage, which necessitates immediate investigation, location and repair.

In considering a vapor-gathering and conservation system, one should further take into account the fact that the components of gasoline evaporated from refinery storage tanks vary considerably, depending upon the characteristics of the gasoline stored and handled. In instances where the finished product contains relatively large amounts of natural gasoline or vapor recovery products saved from still gases, the components of the vapors will be largely butane. Mechanical action will entrain and carry over heavier products which will also breath from the tanks, and if not connected to a conservation system will also be lost. The value of the vapors lost from storage tanks will vary, of course, but if the material in storage is finished gasoline, every gallon lost by evaporation should be calculated at the market price of motor fuel. Of course, if the gasoline is in temporary storage, before stabilizing and treating, some of the losses will not have this value. On the other hand, unblended material, particularly natural gasoline, cannot be included in the vapor conservation system, such as a flexible steel balloon because of its high vapor pressure which makes it imperative that it be stored in pressure vessels.

At locations where surplus butanes are unavailable, the gasoline lost from unprotected storage tanks must be replaced with purchased natural gasoline. Therefore, evaluation of a vapor gathering and conservation system should be on the basis of the quantity of natural gasoline necessary to replace the volatile products lost through evaporation of the lighter components of gasoline.

In certain instances it may be difficult to justify vapor gathering and conservation systems, due to the earnings on such an investment being very low, but it should be remembered that the elimination of evaporation losses is another step toward the conservation of petroleum resources, and is a further improvement of refining art.

It is questionable whether it is economical to install a balloon large enough to prevent all evaporation losses resulting from pumpings in and out of tanks, normal breathing and so forth. For example, the 350,000 cubic foot balloon at Ponca City is connected to one 25,000, three 80,000, and three 66,000 barrel tanks; and on rare occasions the balloon becomes fully inflated. As the vent valves are set at approximately one ounce pressure, when the inside pressure reaches that point, the valves open and permit the escape of vapors to the atmosphere. Such a condition exists only for a short time, and the system soon returns to a balanced condition. To completely eliminate the possibility of any gasoline vapors escaping to the atmosphere from the balloon system would require larger equipment for only small advantages to be gained.

It is difficult to definitely state the amount of evaporation and storage loss decrease resulting from the balloon connected vapor gathering and conservation system because of changed operating procedure and quality of gasoline stored and otherwise handled since the equipment was installed. Comparison of gasoline storage, pumping and loading loss before and after the balloon connected vapor gathering system was installed shows a saving of .55 percent.

The comparison covers a period of four years. Two years before the installation, loss was 1.18 percent, and after it was reduced to .63 percent. Before the installation of the balloon system, the storing and handling of refinery base gasoline involved the addition of purchased natural gasoline and refinery butane enroute to tank cars during loading operations. Since the balloon system was installed, purchased natural gasoline and refinery butane have been added to refinery base gasoline to the extent necessary to meet volatility specifications for the motor fuel, and stored in the balloon connected tanks. Considerable advantage is gained by having available for immediate loading, large quantities of gasoline meeting all specifications, which eliminates the necessity of providing large pressure vessels for seperate natural gasoline storage.

The reduction of .55 percent is equivalent to an annual saving of 27,000 barrels of gasoline, the greater part of which is directly attributable to the balloon-connected vapor-gathering system. There are other types of equipment particularly adapted to the reduction of evaporation losses, and the most economical type of equipment is dependent upon the characteristics of the liquid to be handled, location, and the ultimate "pay-out" of the original investment.

Extrusion, Penetration and Oil Content

Relationships of Greases

*HARRY R. SHAWK

IN recent years considerable attention has been directed toward the development of new testing apparatus and to the improvement of methods used for the classification of lubricants. In the case of liquid lubricants, these improved methods have enabled the refiner to correlate test conditions with service conditions to a greater degree than had been possible formerly. However, in the case of greases and other plastics, the industry has not been so fortunate. Individual refiners have adopted standard procedure used in the control and testing of grease in their own plants, and several procedures have been widely adopted among the refining fraternity, notable among these being the A.S.T.M. cone penetration method.

There are a number of characteristics of grease which have been recognized as being of importance both in control and utilization. These are: (a) consistency, (b) melting point, (c) elasticity, (d) texture, (e) appearance, (f) stability. Of this group, perhaps the greatest single factor of control and utilization importance is that of "consistency."

Klemgard[2] has defined four factors which are believed to determine consistency, namely: yield value, mobility, elasticity and texture. The yield value has been explained by Reiner[6] as being a maximum shearing resistance. If the internal forces which operate on the body are gradually increased to such an extent that the shearing stress at a certain point or a certain region of the body reaches this maximum shearing resistance, the material yields and starts to flow. Mobility has been defined as the ratio between flow and shearing force in excess of that required to start flow, and this is analagous to fluidity, which is the reciprocal of viscosity.

Rhodes[7] has pointed out that although lubricating greases are commonly regarded as plastics, the relationships between unit stress and rate of flow are not exactly those specified by the ideal plastic flow laws. There has been observed no very definite yield point in the case of greases, and in addition, the mobility, or rate of change of deformation to change in stress, has been found not to be constant, but increasing with increasing rates of shear, as pointed out by Arveson[1]. As the stress on a grease is continuously increased by successively decreasing increments, the rate of shear has been found to increase continuously; at first slowly and then more rapidly, until finally a ratio of deformation to stress becomes approximately a constant.

*In the conduct of this research, the author wishes to acknowledge the direction and assistance of Professors M. P. O'Brien and Anders J. Carlson of the University of California.

CONSISTENCY MEASUREMENTS

The standard A.S.T.M. cone-penetration method is without doubt more widely used throughout the industry than any other. Descriptions of this method may be found in the reports of Committee D-2 of the A.S.T.M. in their annual publication, and elsewhere in the literature.

A number of other devices have been developed for measuring the consistency of greases and other plastics. Chief among these are the Abraham Consistometer,[4] Gardner Mobilometer[5] and several viscosimeters developed by Knopf.[3]

Other methods used for consistency determinations include the MacMichael and Saybolt Furol viscosimeters, and various forms of capillary-tube viscosimeters.

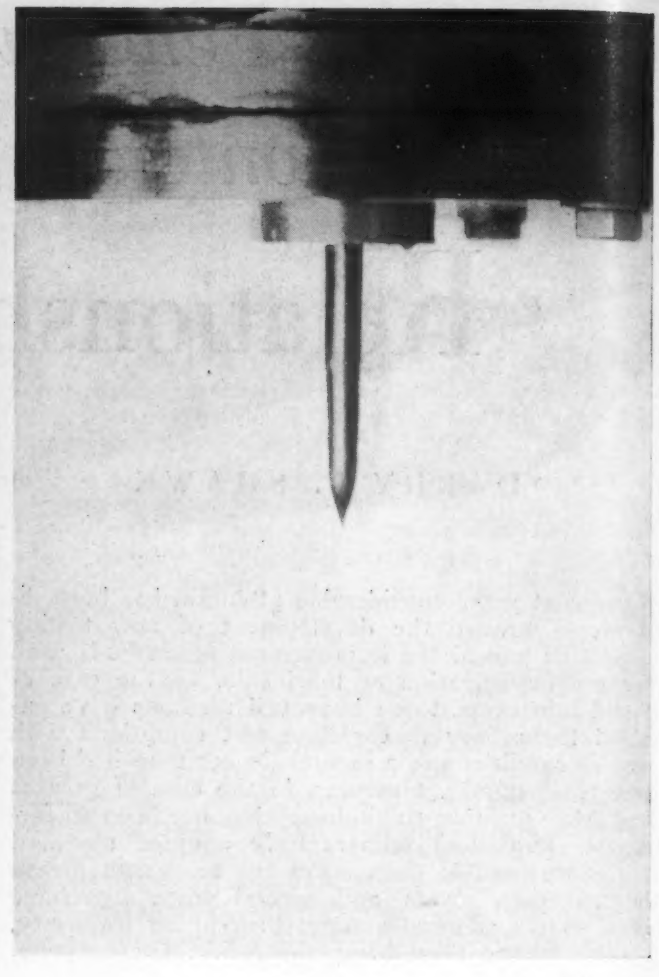
EXPERIMENTAL EQUIPMENT AND PROCEDURE

In reviewing the literature on consistency and its measurement, the author became interested in the possibility of developing inter-relationships between the A.S.T.M. cone-penetration values, so commonly used in the industry, and the extrusion lengths of a number of greases. An apparatus was constructed consisting of a cylinder accurately bored and finished to a 4-inch inside diameter with a length of 12 inches. This barrel was fitted with a piston which was operated from a direct-current motor through a drive mechanism of reduction gears. This gearing gave a 2160/1 speed reduction. The motor was controlled in speed by a potentiometer across the power supply line.

The grease extrusion cylinder was mounted vertically about 8 feet from the floor. The wooden frame supporting the cylinder was equipped with a scale graduated to 0.5 centimeters throughout approximately 250 centimeters of length. By means of this scale it was possible to measure the length of extruded grease.

The test procedure consisted in filling the barrel with the grease sample—about 3 pounds required per charge—taking special care to include as few air pockets as possible. The motor was then started and the grease forced through the ¼-inch sharp-edged orifice. After setting the potentiometer for a given

Sample 3-M



Sample 2-M

velocity, it was found that the motor speed varied not over 1 percent throughout the period required to take six or more check readings.

As the grease was extruded through the orifice, the time was recorded as the lower end passed each 5-centimeter graduation, and the velocity calculated at each point. This velocity was found to be practically constant; the variation being of the same magnitude as the motor speed variation. Thus in the data listed in this article only the averages of the grease extrusion lengths over the entire range of velocities studied are included.

Twelve samples of grease were used, being composed of three grades of four different types of grease. Data was taken on specific gravity, penetration (A.S.T.M. cone method), and extrusion length from the ¼-inch orifice. In addition, on one of the greases (samples 1-S, 1-M and 1-H), the weight of the fractured extruded column was measured, as was the calipered diameter of the column during extrusion. Knowing the extruded length and the specific gravity of the grease, it was possible to calculate the diameter and to compare this with the measured diameter. The diameter by direct measurement was found to be 0.0156 (1/64) inches greater than that of the orifice (0.25 inches), while the diameter calculated from length and specific gravity gave a diameter 0.0150 inches greater than that of the orifice. Hence there seems little if any gain in measuring the weight of the fractured column over measuring the length directly, except perhaps in the lighter grades of grease which have extrusions under 5 centimeters. It is possible to measure the length accurately to within 0.25-cm. which gives an error of plus or minus 5 percent for extrusions of 5 centimeters length. In order to reduce this error, the weight of the fractured column may be determined and converted to length for use in comparative studies.

When fibre greases were extruded at low velocities, premature fracture of the column resulted. As the velocity was increased, the column was found to also increase in length until a velocity of approximately 0.6 centimeters per second was reached. Beyond this value, the extrusion length became independent of velocity of efflux.

A condensed summary of the data used in plotting the curves on the accompanying graphs will be found in Table 1. Each grease type has been designated by a number (1, 2, 3 and 4), and each grease within that type by a letter (S, M or H); the letter "S" designates the softest, "M" the intermediate, and "H" the hardest grease. The table has been made up by grease types, and the greases listed in the order of decreasing hardness within each type. The data in the column labeled "extrusion (cm)" are made up of the average lengths of the extruded column over the entire velocity range studied (up to 1.7 cm/sec. max.), and was usually the result of about 6 different velocity runs. The "mineral oil content (%)" was taken from the refinery specifications for the particular greases.

Penetration and mineral oil content, plotted against each other in Figure 1, exhibit a linear re-

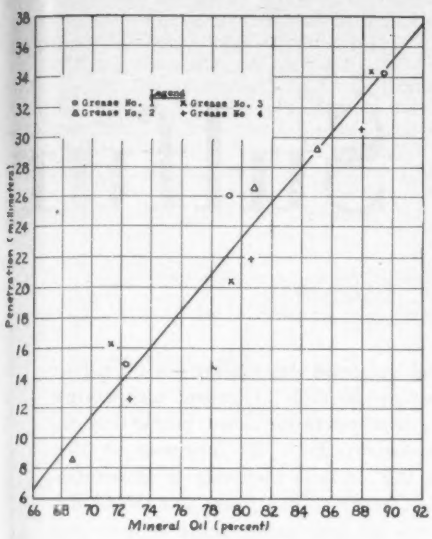


Figure 1
Relation of Mineral Oil Content to Penetration

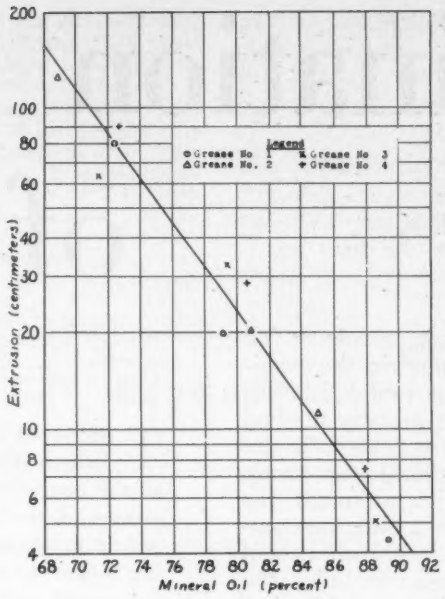


Figure 2
Relation of Mineral Oil Content to Extrusion

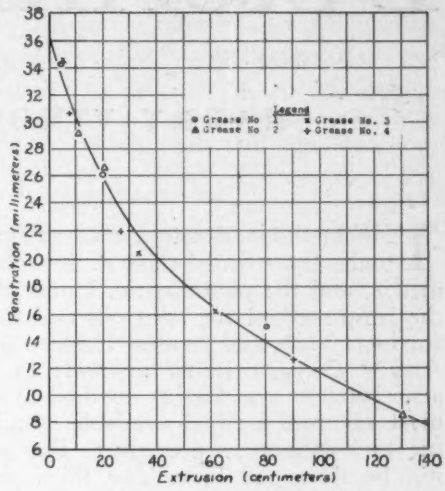


Figure 3
Relation of Penetration to Extrusion

lationship. We may assume that the penetration has been observed with very little error, since each value is the average of a number of different determinations. By inspection of the curve, it may be seen that some of the points lie as much as 4 percent from the average curve. This may be attributed to the refinery variations from the base specifications in order to produce greases of similar consistencies from different batches.

Figure 2 is a semi-log plot of the extrusion against the mineral oil content, and it will be noted that a straight lne may be drawn through the points. The variations of the points from the smooth curve may be attributed to the refinery variations as explained before, except that some allowance must be made for inaccuracies in the extrusions, especially in the case of the extremely soft greases where difficulty was experienced in determining the length due to the short columns produced.

Penetration has been plotted against the extrusion as shown in Figure 3. The maximum deviation of any point from the curve due to errors in extrusion length, and assuming correct penetration, is in most cases less than 10 percent.

TABLE 1

Sample Designation	Penetration (mm)	EXTRUSION (cm)	EXTRUSION (grams)	Mineral Oil (Percent)	Specific Gravity
No. 1—S.....	15.0	80.1	26.5	72.3	0.944
No. 1—M.....	26.1	19.9	6.6	79.1	0.944
No. 1—H.....	34.3	4.4	1.5	89.3	0.944
No. 2—S.....	8.5	130.1	43.1	68.8	0.946
No. 2—M.....	26.6	20.3	6.7	80.8	0.946
No. 2—H.....	29.2	11.2	3.7	85.0	0.946
No. 3—S.....	16.2	63.5	21.1	71.3	0.941
No. 3—M.....	20.4	32.8	10.9	79.3	0.941
No. 3—H.....	34.4	5.1	1.7	88.5	0.941
No. 4—S.....	12.6	90.3	29.8	72.6	0.949
No. 4—M.....	21.9	28.5	9.4	80.6	0.949
No. 4—H.....	30.6	7.5	2.5	87.9	0.949

NOTES—
Grease No. 1—Calcium and sodium base—300 filtered pale oil.
Grease No. 2—Calcium base—100 red and 70 black oils, plus blown asphalt.
Grease No. 3—Sodium base—210 filtered pale oil (fibre).
Grease No. 4—Calcium base—43 steam refined stock.
Cross-sectional area of ¼-inch orifice = 0.0491 sq. in.
= 0.317 sq. cm.

CONCLUSIONS

The studies have indicated that a definite relationship exists between the penetration values obtained by the use of the A.S.T.M. cone penetrometer, and the length of the extruded column required to produce fracture. This relationship is independent of the soap base of the grease, and of the mineral oil used in the manufacture of the grease. It is also shown that the penetration bears a linear relationship to the mineral oil content, regardless of the soap base or of the type of oil used in compounding. Finally, it has been shown that extrusion and mineral oil content may be represented by a straight line when plotted on semi-logarithmic scale.

From Figure 3, it is evident that it is advisable in the case of hard greases, where small penetrations give rise to large errors, to observe the extrusion length of the grease. The rate of change of penetration at this point is decreasing rapidly as the grease becomes harder, while the rate of change of extrusion length is increasing rapidly. The converse is true in the case of light greases since the rate of change of extrusion length becomes small, while that of penetration is increasing.

From the curves in Figures 1 and 2, it is possible to predict the penetration and extrusion for a grease of known oil content, which would be of value in making up greases to meet certain desired specifications. Conversely, from an examination of a grease with respect to its penetration or its extrusion values, it is possible to predict the percentage of mineral oil in the grease quite accurately. This coupled with the general appearance of the grease, which in general determines the soap base, will afford a rapid means of getting an approximate analysis of an unknown grease with respect to soap type and content.

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Determination of Sulfur

HARRY VINOCK

THE rapid and accurate determination of sulfur in petroleum products is of prime importance to the operating, transportation, and marketing divisions of the industry. It is the purpose of this article to discuss the various methods of determining sulfur in oils, their advantages and disadvantages, and methods of increasing their scope; and to describe two methods not in general use.

THE methods of determining sulfur in petroleum fall under three broad classes: the volumetric, the gravimetric, and the photometric. Under the first head falls the lamp method for light oils and the Mabery method for heavy oils and crudes. Under the second falls the ASTM Oxygen Bomb method; to this latter group also belongs the Carius method which although the most accurate method available entails a time-consuming and dangerous procedure. For this reason it will not be discussed here. The third group includes the Turbidimetric method which is merely a modification of the oxygen bomb method.

VOLUMETRIC METHODS

The volumetric methods depend upon a combustion of the sample so that all sulfur present is oxidized to either the dioxide or the trioxide, and the absorption of these products of the combustion in an exactly measured volume of standard sodium carbonate solution according to the following reactions:

$$SO_2 + Na_2CO_3 = Na_2SO_3 + CO_2$$
$$SO_3 + Na_2Co_3 = Na_2So_4 + CO_2$$

The carbonate solution is then titrated, using methyl orange as an indicator, with a standard solution of hydrochloric acid having exactly the same concentration as the carbonate solution to determine the amount of carbonate neutralized by the combustion products. The percent sulfur is then calculated by the following equation:

$$\% \text{ Sulfur} = 100\text{-}CF/W \qquad (1)$$

where: C = cc of sodium carbonate solution neutralized
F = grams of sulfur equivalent to each cc. of the carbonate solution.
W = grams of sample burned.

LAMP METHOD

The latest modified set-up for the determination of sulfur in gasolines, naphthas, and illuminating oils is illustrated diagrammatically in Figure 1. The lamp barrel is calibrated in cubic centimeters, and the adjustable coil shown is used to regulate the size of the flame of the burning oil. The absorber cylinder contains a fretted glass disk as shown upon which rests an exactly measured volume of a standard sodium carbonate solution. The spray trap is connected at C by rubber tubing connections to a suction line which is regulated by means of a suitable valve such as a needle valve.

Solutions required are: Hydrochloric acid—solution containing exactly 2.275 grams of HCl per liter; Sodium Carbonate—solution containing exactly 3.306 grams of Na_2CO_3 per liter; Wash water—distilled water containing approximately 0.004 grams of methyl orange per liter.

Procedure: Close the openings at A and B by means of corks or other means, and introduce into the absorber at D exactly 10 cc of the standard sodium carbonate solution. The carbonate solution will stand on the fretted glass disk without running through as long as A and B are tightly stoppered. Affix the spray trap and turn on gentle suction. Remove the

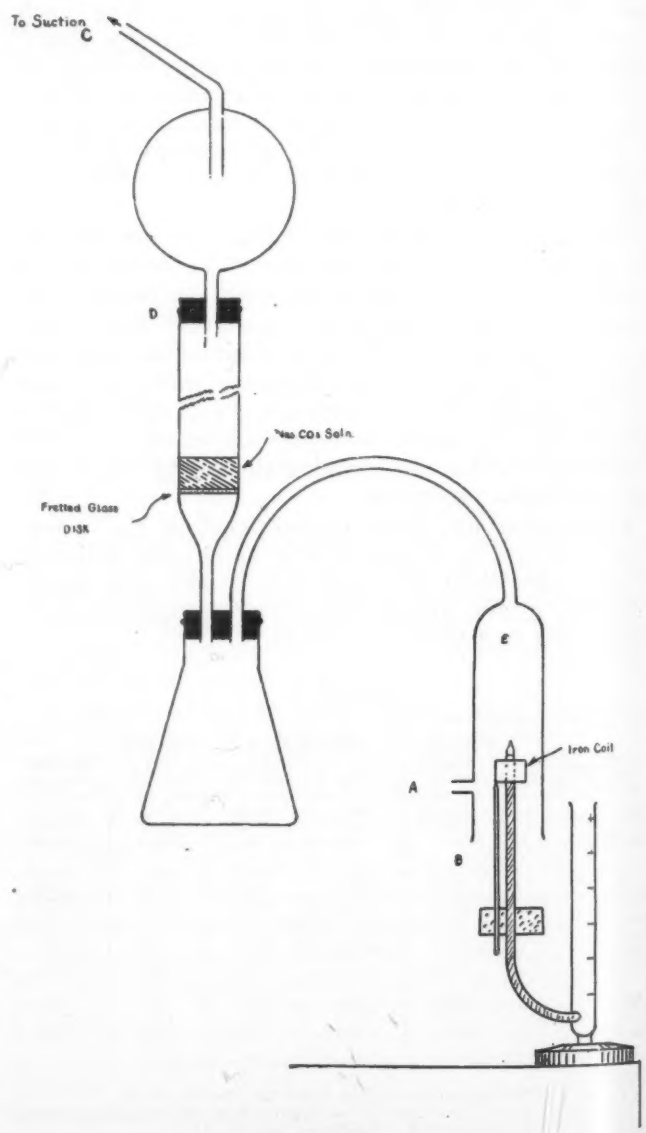

FIGURE 1
Lamp Method

stoppers at A and B. Adjust the suction so that the carbonate solution bubbles vigorously but so vigorously that it tends to go over into the spray top. Fill the clean lamp with the sample to be tested and suck the oil into the wick until the wick is saturated. Fill the lamp barrel to the zero mark. Light the lamp. Adjust the flame by means of the metal coil so that it is steady, free from smoke, and approximately ¼-inch high. Immediately place the lamp under the chimney, E, as indicated in the drawing. Allow the lamp to burn until from 3 to 5 cc. of the oil has been consumed. Extinguish the flame, record the cc. burned, and immediately disconnect the suction. The carbonate solution will then drop into the Erlenmeyer flask. Wash the spray trap and the absorber with the methyl orange wash

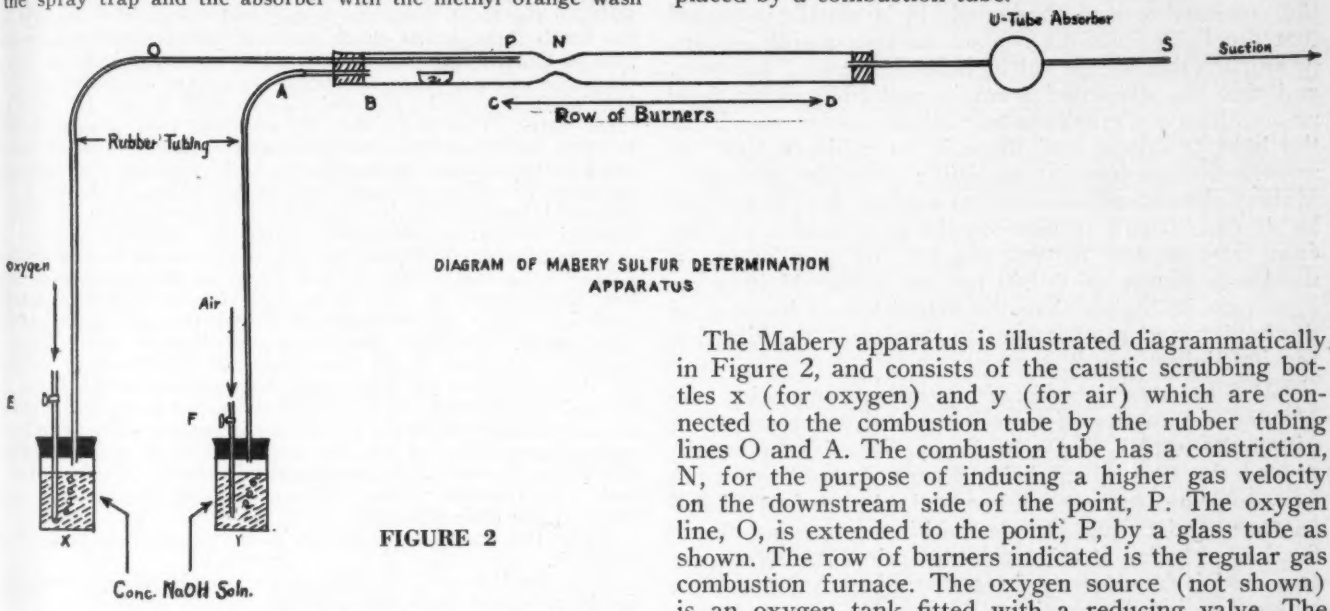

DIAGRAM OF MABERY SULFUR DETERMINATION APPARATUS

FIGURE 2

water until the washings no longer show pink. Titrate the washings with the standard HCl solution. The percent sulfur is calculated by this variation of equation (1):

$$\% \text{ Sulfur} = 0.1\ C/W = 0.1\ C/VG \qquad (2)$$

Where: V = volume of oil burned.
G = specific gravity of oil calculated from the A.P.I. gravity .

For light oils this method is ideal and gives very good accuracy to the second place although the third figure is doubtful. Its advantages are simplicity, and the fact that the procedure requires a minimum of attendance during the burning of the oil. However, as outlined the method is not applicable to such samples as gas oils, furnace oils, etc., because these oils are not volatile enough to burn without smoking in a lamp. However, by diluting these oils with a diluent of known sulfur content, such as a light gasoline, they can be run successfully on the lamp with an accuracy to the second place equaling that of any other method commonly used. In such cases the calculation for the percent sulfur assumes this form:

$$\% \text{ Sulphur} = 0.1\ (C - D)/VG \qquad (3)$$

Where D = cc of carbonate neutralized by diluent

Sample calculation:

A gas oil of 0.8 sp. gr. is diluted 1 to 1 with a gasoline that neutralized 0.1 cc. of standard sodium carbonate solution per cc. of the gasoline burned. Four cc. of the mixture is burned. Ten cc. of standard sodium carbonate solution was used in the absorber, and 5 cc. of the standard hydrochloric acid solution was required to titrate the washings.

Since there is a 50-50 mix, there are 2 cc. each of the gas oil and gasoline burned.

C = (10 cc of carbonate − 5 cc of hydrochloric acid) = 5 cc.

D = (2 cc of gasoline x 0.1 cc of carbonate soln.) = 0.2 cc.

$\%$ Sulfur $= 0.1\ (5 - 0.2)/2 \times 0.8 = 0.30$ per cent.

This dilution method was used on a great variety of gas oils and light fuel oils, and the results checked against the ASTM oxygen bomb method to the second place. However, the dilution method cannot be used with dark oils containing appreciable amounts of suspended carbon as these oils smoke, coke, and tend to give low results. Its use with crudes is also inadvisable.

MABERY COMBUSTION TUBE METHOD

The Mabery method can be used on all oils except gasolines and naphthas. It is essentially an extension of the lamp method for heavier oils with the lamp replaced by a combustion tube.

The Mabery apparatus is illustrated diagrammatically in Figure 2, and consists of the caustic scrubbing bottles x (for oxygen) and y (for air) which are connected to the combustion tube by the rubber tubing lines O and A. The combustion tube has a constriction, N, for the purpose of inducing a higher gas velocity on the downstream side of the point, P. The oxygen line, O, is extended to the point, P, by a glass tube as shown. The row of burners indicated is the regular gas combustion furnace. The oxygen source (not shown) is an oxygen tank fitted with a reducing valve. The suction source must be constant, and may be a vacuum line, aspirator pump, or aspirator bottle. The U-tube absorber holds exactly 10 cc. of the standard sodium carbonate solution.

Solutions: Same as for lamp method.

Procedure: Light all the burners from C to D, and allow that portion of the combustion tube to become hot. Weigh out 0.2 to 0.3 grams of the sample into the porcelain boat, z. Place the boat in the combustion tube midway between the left end and the constriction as shown. Regulate the valves E and F so that air and oxygen are bubbling moderately through the U-tube absorber; approximately twice as much oxygen as air is bubbling through their respective caustic scrubbing bottles. Light the two end burners at B. Vigorously heat the point, P, with a Meeker burner held in the hand. The vapors rising from the sample and carried forward by the air stream should now ignite at P and burn with a blue, smokeless and steady flame at that point. Maintain the flame at P by judicious manipulation of the valves E and F. As the flames tend to die down, light more burners progressively from B to C as needed until nothing but carbon remains in the porcelain boat. Quickly switch the oxygen and air leads at the caustic wash bottles, and complete the combustion in the direct current of oxygen. Carefully detach the U-tube containing the standard carbonate solution so as not to lose any of the liquid. Titrate the carbonate while still in the U-tube with the standard HCl using Methyl Orange as the indicator. Percent sulfur is calculated by equation (2).

The advantages of the Mabery method may be summed up under one head, speed. A skilled operator can complete a Mabery run in from 45 minutes to an hour depending upon the nature of the sample as compared to the from 6 to 16 hours necessary for an oxygen bomb determination. Under very favorable conditions a series of Mabery runs can be run at an average of 30 minutes per run.

The disadvantages are numerous. They are:

(1) *Doubtful accuracy.* Even the statistical accuracy when the titration is carried out with a burette calibrated in 0.1 cc. is not better than two places, and the actual accuracy is even less. Check runs of a sample showing 0.33 percent sulfur by the oxygen bomb

method will on the Mabery give results varying from 0.27-0.33 percent when made by the same operator, and 0.26-0.36 percent when made by different operators. Again, there is no guarantee that some of the sample escapes unburned before the flame is established, or that all the sulfur is burned to the oxides, or that all the sample is completely oxidized even after the flame has been established. A series of runs usually fouls the U-tube and the ends of the combustion tube with a scum of unburned oil no matter how carefully the the combustion was conducted. It is usually assumed that the light fractions contain no appreciable amount of sulfur (that all the sulfur is in the heavy fractions), and that the unburned scum is negligible. Both these assumptions are unwarranted; all the sulfur may be in the light fractions, and there is no evidence that the unburned scum contains negligible quantities of sulfur. Mabery determinations checked against ASTM oxygen bomb determinations consistently give results varying from 0.04 to 0.10 percent too low, or even more. In the lower ranges of 0-0.40 percent sulfur Mabery results may be higher than the actual values because of the habit of most operators to "squeeze" the titration for its highest result.

(2) *The need of skilled operators.* Operating the Mabery is a matter of experience, and, some say, even of mumbo-jumbo. The procedure varies with the weather and the type of oil being tested. A crude presents one problem, a gas oil another, and a heavy fuel oil still another. And no two samples within any general classification act alike. It takes time to train a Mabery operator, and if he does not keep operating the apparatus, he tends to lose his touch.

(3) *Intellectual dishonesty of the operator.* This is the tendency of the operator to get what he is supposed to get, and of not calling the results as he sees them. The aforementioned "squeezing" of the titration is a flagrant example. With a method such as the Mabery upon which a great many routine tests are run the temptation to intellectual dishonesty is very strong. An extreme example of this tendency concerns an operator who worked out a system of additive "factors" to correct the inherent inaccuracies of the method. These "factors" varied with the kind of oil (crude, gas oil, heavy fuel) and with the different sub-varieties of each general classification. If a crude ran 0.26 percent sulfur, the factor was 0.04 percent; if the same crude ran 0.28 percent sulfur, the factor was 0.02 percent. However, in the case of a crude that gave 0.86 percent sulfur, the factor became 0.14 percent except in cases when the Mabery result gave 0.82 percent when the factor became 0.18 percent. It was only a coincidence that the "factor" in every case was the difference between the Mabery results and the results which were usually obtained for the various samples by the ASTM oxygen bomb method.

OXYGEN BOMB METHOD

The ASTM oxygen bomb gravimetric method gives the most accurate means for the determination of sulfur usually available for refinery use. Its error must be within ±2 percent of the sulfur found, and is usually less. The bomb is constructed of a metal resistant to the physical and chemical conditions of the test; the metal is usually the Illium alloy. Essential parts of the bomb (Figure 3) are:

The cylinder or bomb proper, 1A
The cover, 2A, held in place by
The screw cap, 3A
The supporting rods, 4A and 5A, for the
Fuel tray, 43A, which are also the electric terminals for the fuse wire, 45C. The check valve, 11A.

Procedure: Place 20 cc of distilled water in the bottom of the bomb. Weigh accurately to the 0.1 mg from 0.6 to 0.8 grams of the sample directly from its container into cup, 43A. Attach fuse wire, 45C. Place cup with sample in position shown with fuse wire dipping into the oil. Close bomb tightly. Fill the bomb slowly with oxygen to a pressure of 35 atmospheres. Ignite the charge by attaching one wire from the firing circuit to the insulated terminal, 8A, and touching the other wire to the body of the bomb. Immediately immerse the bomb in a bucket of cold water and allow it to stand for 10 minutes. Remove the bomb from the water, and release the oxygen in the bomb through the check valve at an approximately even rate so that the pressure is reduced to atmospheric in not less than one minute. Open the bomb and rinse all parts of the interior including the top and oil cup with a fine jet of distilled water. Filter and collect all washings (not to exceed 350 cc) in a beaker. Add 2 cc concentrated HCl and 10 cc of saturated bromine water to the filtrate, and evaporate the solution to about 75 cc on a steam bath or hot plate. Add 10 cc of saturated barium chloride solution in a fine stream or dropwise to the hot solution. Stir during the addition and for 2 minutes afterwards. Allow the solution to stand for 12 or for 1 hour on a steam bath or hot plate (in the latter case the precipitate should be allowed to settle for another hour while cooling). Filter the supernatant liquid through quantitative filter paper. Wash the precipitate with distilled water by decantation and then on the filter paper till chloride free. Transfer the precipitate and filter paper to a suitable weighed crucible and dry them at low heat until the paper is charred. Ignite at a good red heat till the precipitate is burned white. The best way to accomplish the complete ignition is to place the crucible containing the wet filter paper in a cold electric muffle furnace and to turn on the current. Drying, charring, and ignition will occur at the desired rate.

Allow the crucible to cool to room temperature, and then weigh it.

From the increase in weight of the crucible the percent sulfur is calculated from this formula:

$$\% \text{ Sulfur} = \frac{\text{Grams } BaSO_4 \times 13.734}{\text{Grams oil used}}$$

The chief advantages of the oxygen bomb-gravimetric method are: accuracy, and the simplicity of the

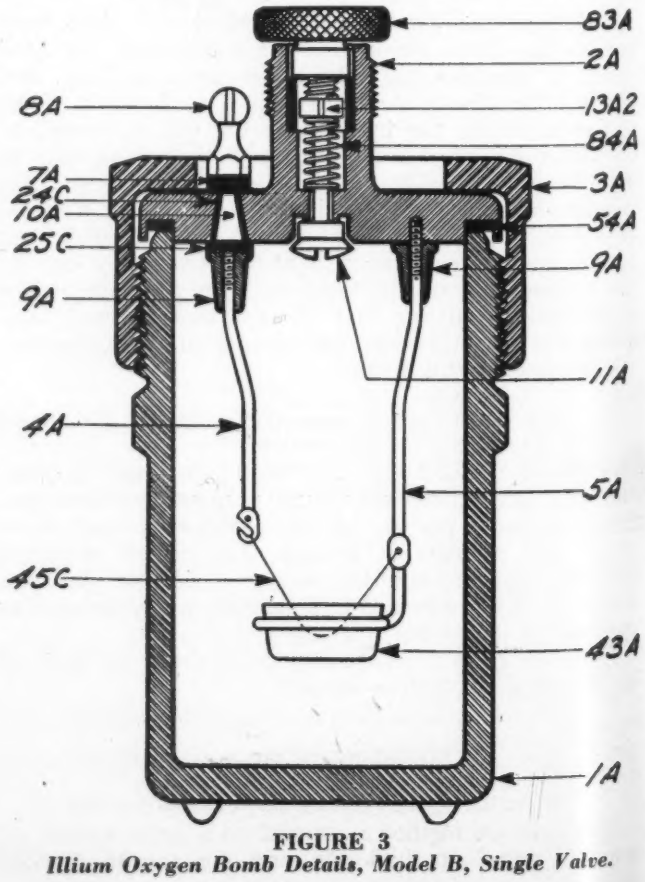

FIGURE 3
Illium Oxygen Bomb Details, Model B, Single Valve.

manipulations which do not require any special skill beyond the usual laboratory technique. Its chief disadvantages are: the length of time necessary for the determination which varies from a minimum of 6 hours to a maximum of 16 hours, and the possibilities of errors occurring during the ignition of the precipitate.

PHOTOMETRIC METHOD

The chief photometric method for the determination of sulfur in oils is the Turbidimetric. The method requires: first a combustion of all the sulfur in the sample by the oxygen bomb method, and then the determination of the sulfur in the form of barium sulfate photometrically by means of the turbidimeter. The turbidimetric principle depends upon a suspension of barium sulfate preventing the direct passage of light from a source of constant brilliance through a column of solution. The concentration of sulfur present as barium sulfate varies inversely as the depth of the solution necessary to make invisible the filament of a lamp at a given voltage.

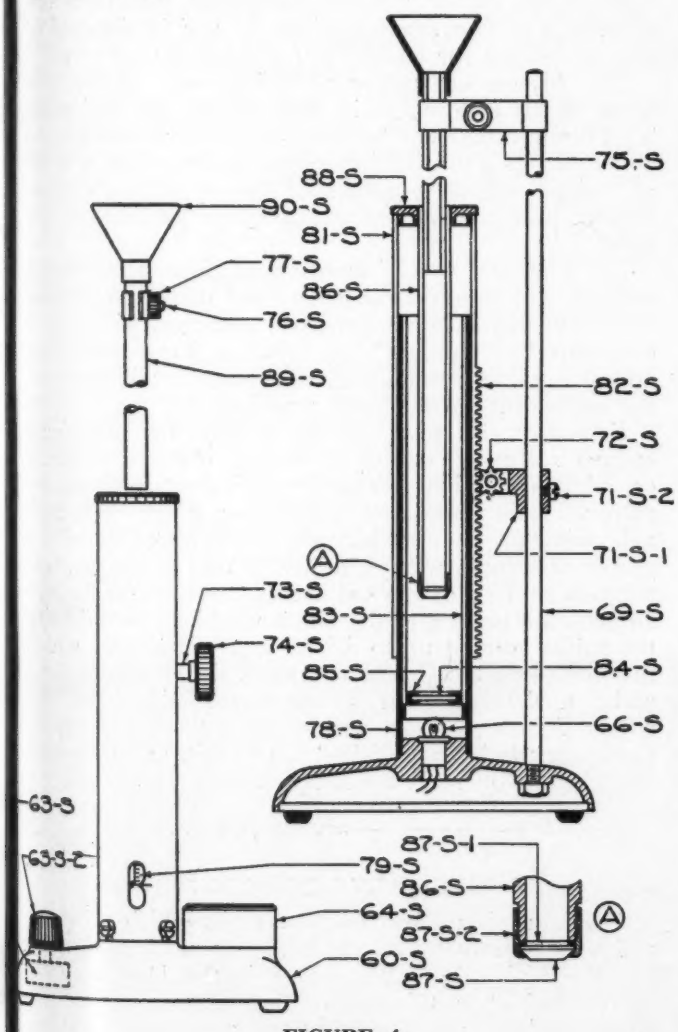

FIGURE 4
Details of Turbidimeter.

The Turbidimeter (Figure 4) consists of a bakelite-walled tube (83S) having an optical glass bottom (84S) in which the test solution is placed; a plunger tube of similar construction by which the effective depth of the solution is measured (86S); a gear, rack, and telescope tube mechanism for adjusting the position of the plunger; an eye-tube and soft rubber eye-piece; and a lacquered metal base on which is mounted the electric filament lamp (66S) on which the eye is focused, a rheostat (63S) for controlling the filament voltage, and a voltmeter (64S) for indicating that voltage.

In operating the tubidimeter for sulfur determinations special barium chloride crystals of specified grain size (20-30 mesh) are introduced into the test solution causing a finely divided precipitate of barium sulfate. This precipitate will remain in suspension long enough

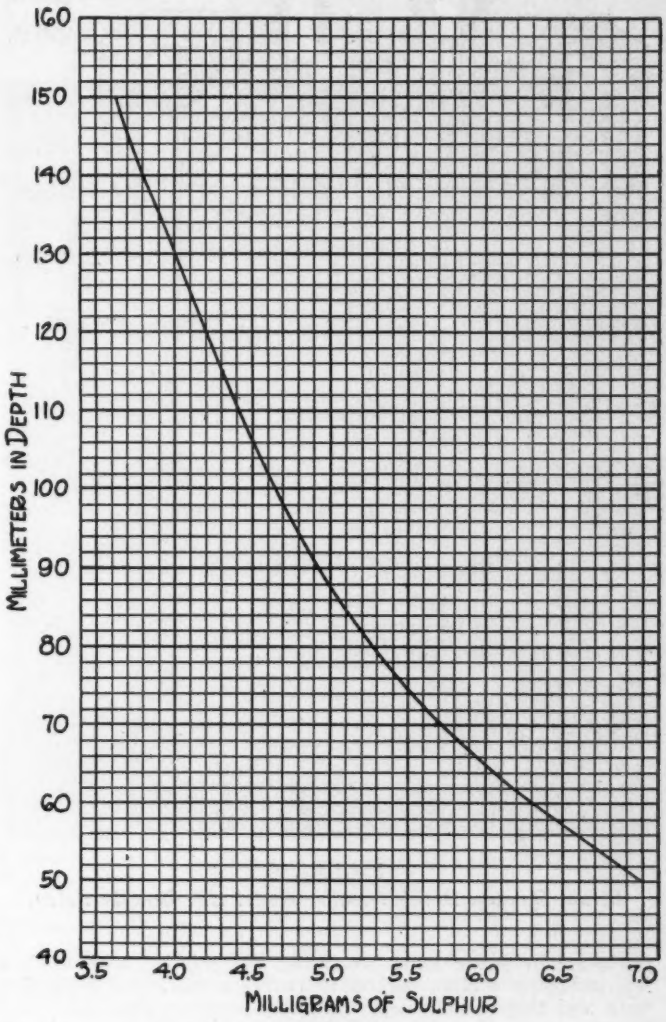

FIGURE 5
Sulphur Chart.

for several check determinations. The turbid solution is poured into the solution tube which is placed in position and the plunger tube is run to the bottom of the solution tube by the rack and pinion mechanism. With the filament voltage set at a predetermined point, and the eye-tube lowered into the plunger tube, the operator raises the plunger until the filament exactly disappears, leaving only a field of diffused light. The distance between the bottom of the solution tube and the bottom of the plunger tube is then read directly on a millimeter scale mounted vertically on the instrument (79S). Several check readings may be made, or the end point may be approached from both directions, i.e., by lowering the plunger tube from the top until the lamp filament appears. Check results are consistently uniform even among different operators. A calibration curve (Figure 5) is provided for converting the turbidimeter reading to milligrams sulfur present.

Procedure: Make an oxygen bomb combustion using an oil sample of from 1-1.5 grams as for the gravimetric method. After the inside of the bomb has been thoroughly washed, add 2 cc of concentrated HCl and 10 cc of saturated bromine water to the washings. Evaporate the washings to about 75 cc on a

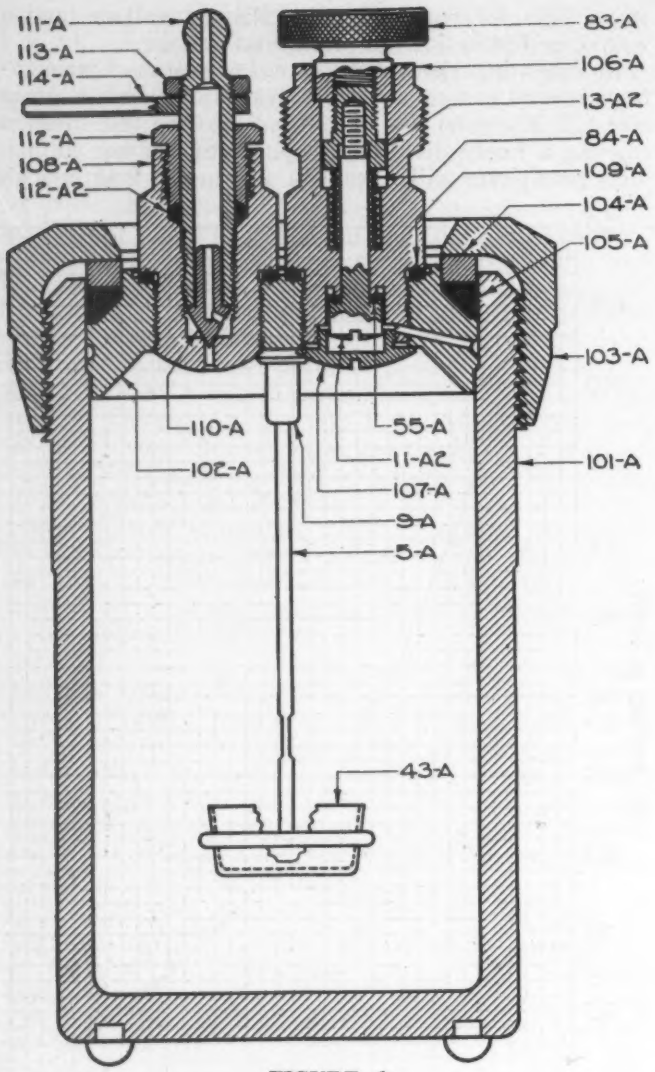

FIGURE 6
Illium Oxygen Bomb Details, Model BB, Double Valve.

hot plate or steam bath. Neutralize the solution with sodium hydroxide or sodium carbonate (using methyl orange indicator) and then acidify with ½ cc of concentrated HCl. Add approximately 15 grams of C.P. sodium chloride, and make up the solution to exactly 150 cc with distilled water.

Since the turbidimeter scale gives reading only within the range of 50-150 millimeter, a proper portion of the 150 cc based on the approximate percent of sulfur in the original sample must be taken to make the readings fall within that range. If the percent sulfur is totally unknown, this portion must be determined by trial and error. If the sulfur content can be approximated, the following table may be used in determining the volume of solution to be taken when 1.5 grams of the oil has been used in the bomb

% Sulfur	Cc of sample to be taken
0.26 — 0.46	150
0.43 — 0.76	90
0.66 — 1.17	60
1.00 — 1.66	40
1.33 — 2.33	30

To the above indicated sample is added in an Erlenmeyer flash enough distilled water to make a total of *exactly* 200 cc. One measure (a scoop provided with the turbidimeter) of barium chloride crystals is added; the flask is stoppered, and shaken vigorously for about one minute. The turbid solution is then placed in the turbidimeter solution tube (83S). After pouring the 200 cc of the turbid solution into the instrument, the plunger (86S) should be inserted in the solution tube and the eye-tube (89S) and eye-shield (90S) placed in position. The voltage is adjusted by the rheostat to exactly 3 volts as indicated on the voltmeter. The depth of the solution is varied by the movement of the adjusting wheel (74S) and the end point taken at complete disappearance of the filament. The reading in millimeters is read off the scale (79S). Two or three readings should be taken to obtain an average.

Milligrams sulfur in the volume of solution in the turbidimeter are read of the calibration curve (Figure 5). Percent sulfur is then calculated by the following formula:

$$\% \text{ Sulfur} = \frac{(150\text{ cc})}{X} \cdot \frac{M}{1000} \cdot \frac{100}{W} = \frac{15\,M}{X\,W}$$

Where: M = milligrams sulfur from turbidimeter reading
X = cc of 150 cc portion used in instrument
W = weight of sample of oil in grams.

Note: This photometric method can be used only for samples containing down to 0.26 percent sulfur if 1.5 grams of the oil are ignited. A method of avoiding multiple ignitions when the sulfur content is below 0.26 percent will be outlined below.

The advantages of the bomb-turbidimetric method are: Speed—the test can be run in one hour or less; accuracy—comparable to the gravimetric method; convenience and simplicity of the procedure—satisfactory results can be obtained by unskilled operators after a few trials.

The disadvantages of the method are:

(1) *The necessity of knowing the approximate percent sulfur before the test* altogether this is a disadvantage of convenience primarily, and in the case of routine testing for control is no disadvantage at all.

(2) *Errors—or rather variations*—caused by personal visual differences in determining the end-point. This disadvantage can be easily overcome by each operator calibrating the full instrument scale against a series of sodium sulfate solutions of known sulfur concentration. Figure 5 is a calibration curve for normal eyesight.

(3) *The necessity of multiple ignitions* when testing samples with a sulfur content of less than 0.26 percent. This difficulty is more apparent than real and can be overcome by "padding" the solution. This consists of adding enough sodium sulfate solution of known sulfur equivalent to the bomb washings.

Example: Dissolve 4.4310 grams of anhydrous sodium sulfate in exactly 1 liter of distilled water; 1 cc. of this solution is exactly equivalent to 1 mg. of sulfur. If we have a sample whose sulfur content is approximately 0.1-0.2 percent, the ignition from 1.5 grams of sample will yield 1.5-3.0 mg. of sulfur. The addition of 4 cc. of the sodium sulfate solution through an accurate burette to the bomb washings would bring the sulfur content up to 5.5-7.0 mg. which falls within the turbidimeter's effective range. Now suppose we make a determination as previously described and obtain 5.58 mg. total sulfur; the sulfur attributable to the sample is then (5.58-4.00) = 1.58 mg. of sulfur. The percent sulfur in the sample would then equal

$$\frac{0.00158 \times 100}{1.5} = 0.105 \text{ percent}$$

DOUBLE VALVE BOMB METHOD

A volumetric method for heavy oils which preserves and even accentuates all the Mabery's advantages without the Mabery's disadvantages is the Double Valve Bomb Method. In this method the combustion tube and all its gadgets and complications are replaced by an oxygen bomb having a double valve cover (Figure 6). After the ignition of the proper sized sample (up to 1.5 grams), the products of the combustion are slowly vented from the outlet valve (111A) through an absorber containing a measured volume of standard sodium carbonate solution. Any residual gas scavenged out of the bomb by the introduction of fresh oxygen through the inlet valve (106A). The absorber solution is then titrated with standard hydrochloric acid (methyl orange indicator) as in the other volumetric methods, and the percent sulfur is calculated by equation (1).

Improved Efficiency at Lion's *New Filtration Plant*

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THE petroleum industry desired some improvement in the mechanics of filtration for the handling of clarification problems. Since the acceptance of the contact filtration process the industry almost unanimously has used the Sweetland pressure filter for the separation of filter clay from lubricating oil stocks. In general the improvements made on this press since the beginning of contact filtration have been labor-saving devices of minor importance. As for the quality of filtrate, the influence of any or all improvements has been practically negative. The adoption of monel metal cloth replacing the canvas-covered filter leaf may have reduced maintenance costs with high temperature filtration, but the yield was still a filtrate requiring after-clarification to free it of clay fines. The development of the Oliver precoat vacuum filter offers an improved method of clarification.

The precoat filter installation at the Lion Oil Refining Company plant in El Dorado, Arkansas, operates continuously for a period of seven days, requiring no attention over this period, other than for the disposal of spent clay. From the beginning of the cycle to the end the filtrate is entirely free of solids; no after filter clarification is required. Perhaps the most promising performance feature is the ratio of actual plant loss of lubricating stock to spent clay which over a two-month period measures slightly less than one-half of one percent of the charge to the filter. This installation is processing an intermediate lube distillate measuring approximately 68 seconds S. U. viscosity at 210° F. The stock is filtered without dilution and no naphtha wash of cake or any other oil recovery process is used.

The end panel is removed showing troughs leading to the scroll conveyor.

Installation of the precoat vacuum filter.

In general appearance the precoat filter resembles the standard continuous filter. The major differences are in the way a filter aid is used and in the cake discharge. The operating cycle consists of two phases—precoat formation and clarification.

PRECOATING THE FILTER

High flow rate diatomaceous earths are used for precoat formation. This material, commonly known as filter aid, is mixed into a slurry with a non-viscous petroleum fraction. Either gas oil or filtrate blended with naphtha will make a satisfactory slurry. The slurry is fed into the filter tank in which a monel metal cloth covered

cylindrical filter drum revolves. Vacuum applied to the drum builds upon the filter surface a cake or "precoat" of filter aid. The precoat operation required approximately one hour off stream for building a cake of 2-inch thickness.

CLARIFICATION

The oil to be clarified is then fed into the filter tank where a liquid level is maintained. Constant vacuum on the rotating drum filters the oil through the precoat, leaving a layer of solid (filter clay) on the precoat surface. As the drum surface leaves the oil level, drying of cake starts and continues to the point of discharge. The discharge of filter clay is accomplished by means of an advancing knife edge which shaves off the clay layer, together with a thin film of the filter aid; thus a fresh surface of precoat is presented for further clarification with each revolution of the filter drum. The spent clay is removed from the filter by means of a scroll conveyor.

There are a number of points of flexibility about the assembly which enable operation changes to be made to meet various conditions encountered in the processing of different type stocks. The throughput rate of the filter can be controlled in four ways: (1) By varying the rotating speed of the filter drum; (2) by varying the liquid level, that is, the degree of submergence of filter drum in the oil; (3) by varying the filtration temperature; and (4) by the amount of vacuum applied to the filter drum.

DESCRIPTION OF UNIT

The precoat vacuum filter installed at this plant is a 5x4-foot unit, having approximately 65 square feet of filter surface. A 5-horsepower electric motor is mounted on the unit to drive the drum and agitator for maintaining a homogeneous suspension of the slurry. A 3-horsepower motor operates the clay discharge scroll conveyor. Vacuum is maintained by means of a dry vacuum pump. This is a reciprocating feather valve type pump, 14-inch cylinder and 8-inch stroke, and it is driven by a 20-horsepower electric motor. A receiver is installed between the filter and vacuum pump for separation of liquid from the gas entering the vacuum pump.

With this installation, hot flue gas direct from a furnace stack was supplied to the filter in preference to atmospheric temperature air. This feature of construction was included to insure dryest possible cake and to safeguard against possible oxidation of filtrate. However, numerous test runs made using atmospheric temperature air showed no impairment of filtrate and no measurable increase of oil loss in spent clay.

Operating at a drum speed of 2.5 minutes per revolution and at 36 percent filter drum submergence and with charging stock at temperature of 300 to 500° F., the filter has a filter rate capacity of 16 gallons per square foot per hour. The knife advance into the precoat is .0004 of an inch per revolution of the filter drum. At the start of the 7-day filtration period the precoat thickness is about 2 inches. At the end of the period the precoat is about ¼ inch thick. The filter rate throughout the period is constant and at no time does the filtrate show any trace of solids. Operations at the 55 percent permissible drum submergence indicate a full capacity of 22 gallons per square foot per hour may be expected.

The lubricating stock processed with this installation is 68 seconds S. U. viscosity at 210° F. acid-treated distillate. Activated filter clay of high efficiency is used. Due to the small amount of clay required (5 pounds per barrel of oil) and the low loss of oil to clay encountered, no attempt is made to reclaim the oil from spent clay.

As the operation is continuous and the various phases of the cycle are performed automatically, there is very little variation in the results obtained. The following tabulation is an average of 359 hours of operation:

Temperature of feed, °F.	242
Temperature of gas in filter hood, °F.	168
Operating vacuum (BG)	21″
Drum speed, min. rev.	2.5
Filter aid consumption, lbs. per bbl. oil	.04
Filtrate rate, gals. per sq. ft. per hr. (based on total area and 36% drum submergence)	16
Oil loss in filter cake, percent by weight of cake	27.23
Net oil loss, gals. per bbl. stock charged	.195
Net oil loss to stock charged, percent	.470

Further reduction of the drum speed and consequent reduction of filter aid consumption as shown in the following tabulation which is an average of 44 hours operation, did not lower filter rate, and it is believed that a still lower drum speed is practical. While the rate shown below is slightly higher than at the greater drum speed, it is believed that an average over a longer period would not show a substantial increase over the 16-gallon rate for the 2.5 minutes drum speed:

Temperature of feed, °F.	261
Temperature gas in filter hood, °F.	188
Operating vacuum (BG)	17″
Drum speed, min. rev.	3.5
Filter aid consumption, lbs. per bbl. oil	.025
Filtrate rate, gals. per sq. ft. per hr. (based on total area and 36% drum submergence)	18.1
Oil loss in filter cake, percent by weight of cake	26.90
Net oil loss, gals. per bbl. stock charged	.192
Net oil loss to stock charged, percent	.458

For contact filtration of bright stocks or oils considerably heavier than that processed at this refinery, it may be advisable to install some means for recovering oil from spent clay.

Test results obtained from the operation of an experimental precoat filter of laboratory size have shown that bright stocks can be filtered without dilution. But if it is desired to filter in naphtha solution, lower vacuum can be employed and the cake washed by means of a naphtha spray before reaching the discharge zone. If high solvent losses are encountered, the gases from the vacuum pump can be exhausted through a condenser or absorber to minimize the loss.

Another method for oil recovery is to filter the stock at high temperatures without dilution and drop the spent clay into a tank of naphtha or other solvent which is to be used in the dewaxing process. The slurry of spent clay and solvent can then be charged to a second filter from which the spent clay could be disposed of in the conventional manner. An idle press could of course be utilized for this job. However, a small vacuum filter operating under low vacuum, with the discharge blade stationary, should do this reclamation job continuously without the inconvenience of intermittent pressure operation.

It is conservatively estimated that such an installation would reduce by 50 percent the labor costs of the average bright stock contact plant, practically eliminate solvent losses, and yield a filtrate entirely free from suspended solids.

Kansas Gasoline Plant Has Interesting Features

WHEN Natural Gasoline Corporation, a subsidiary of Warren Petroleum Company, began construction of its new plant near McPherson, Kansas, in the summer of 1936, the gas processed was to be handled with natural pressure. However, due to changing methods in the field which provided a considerable volume of gas from separators at the wells, it was necessary to install compressors during October of that year.

The plant was built by using practically all new material, and includes a new departure in gas-engine drive with compressor hook-up. The engines installed are of the 8 cylinder-in-line vertical, L head cylinders, with 2 rows of 5 each. Due to the compactness of the design, each unit occupies approximately 140 square feet of area. With a floor space of 10 x 14 feet for each engine, the company was able to install the 10 machines, totaling 2600 horsepower in an unusually small building.

Thirty-two wells have been connected to the plant gathering lines, seven of which produce gas with sufficient pressure that it can be processed with natural pressure, and the seven wells so hooked up produce approximately 10,112,000 cubic feet of gas. The remainder of the wells are handled in the field under low pressure, and five of the engines in the plant bring the 6,058,000 cubic feet into the yard under an intake vacuum of 12 inches mercury. The gas varies in gasoline content, and the plant production is governed by the kind of gasoline manufactured, but when the schedule calls for a product having a vapor pressure of 14 pounds, Reid, the average volume manufactured is about 10,700 gallons daily.

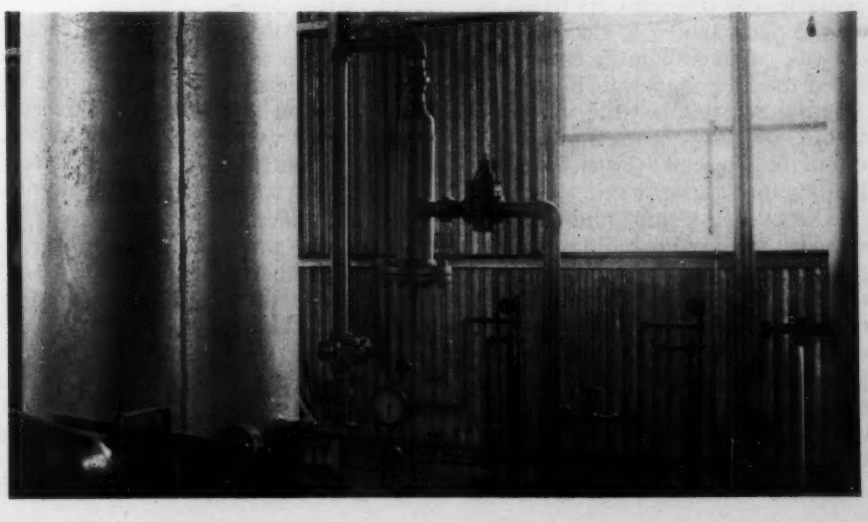
The south row of five 260-horsepower engines is used as field machines, bringing the gas in from the field and compressing it to the required pressure for absorption, while the remaining five machines are used to boost the residue gas to a pressure sufficient that it can be introduced into gas pipe lines. One of the five machines handling stripped gas is equipped with a gas cylinder to handle the vapors from accumulator drums for recompression and condensation of the propane, butane and heavier fractions which may have escaped from the vessels.

ABSORPTION UNIT

The absorption part of the plant was constructed of usual type of low-pressure units, and the distillation equipment follows lines laid down by the majority of gasoline manufacturers in the Mid-Continent oil fields. Pressures maintained upon the absorber averages about 44 pounds, gauge, with mineral seal oil utilized for absorption of the gasoline. The usual exchangers and preheaters are used in the system to obtain exchange of heat and prepare the rich oil for processing in the distillation unit.

Water is produced on the premises from deep wells by using deep well electric-driven pumps, and circulated over louvre towers. Adequate cooling of the cooling water is obtained when water to the tower runs about 80° F. and returns from the cooling basin at about 60° F. All water is handled by motor-driven centrifugal pumps placed in the regulation pit so a constant head will be maintained upon the suction lines.

Three principal products are manufactured at this gasoline plant; natural gasoline, butane and propane. Fractionators are installed to cut any marketable product of natural from 10 pound to 26/70, or higher vapor pressure if necessary. The raw product has a vapor pressure of about 45 pounds, Reid, due to the desire to absorb all the available butanes and propane contained in the wet gas. The usual operation of the stabilization unit is such that a natural product of 14 pounds is manufactured, leaving a considerable volume to proc-



Partial view of Warren Petroleum Company's Galva Gasoline plant Cupric Chloride "copper treater" showing inlet of sour gasoline and air to treater drum at left. Manometer at left used across ⅛-inch orifice to maintain 1-inch differential of air entering gasoline for reaction of oxygen with treating compound.

ess for butane and propane. The main fractionator column is operated 290° F. and at 175 pounds when making the usual 14-pound product, with the overhead condensed and passed through the auxiliary column for butane and propane production.

Gasoline processed from the distillation apparatus is carried as vapor to enclosed shell-and-tube condensers and after-coolers for liquification, and those vapors not condensed to a liquid are passed to the recompressor for finishing. The composite production, absorption natural and recompressed vapors are all fractionated in the main column for separation of the desired cuts. Stabilized natural, of whatever grade desired and manufactured, is treated to a sweet and non-corrosive product continuously in what is commonly called a "copper sweetener" before being stored.

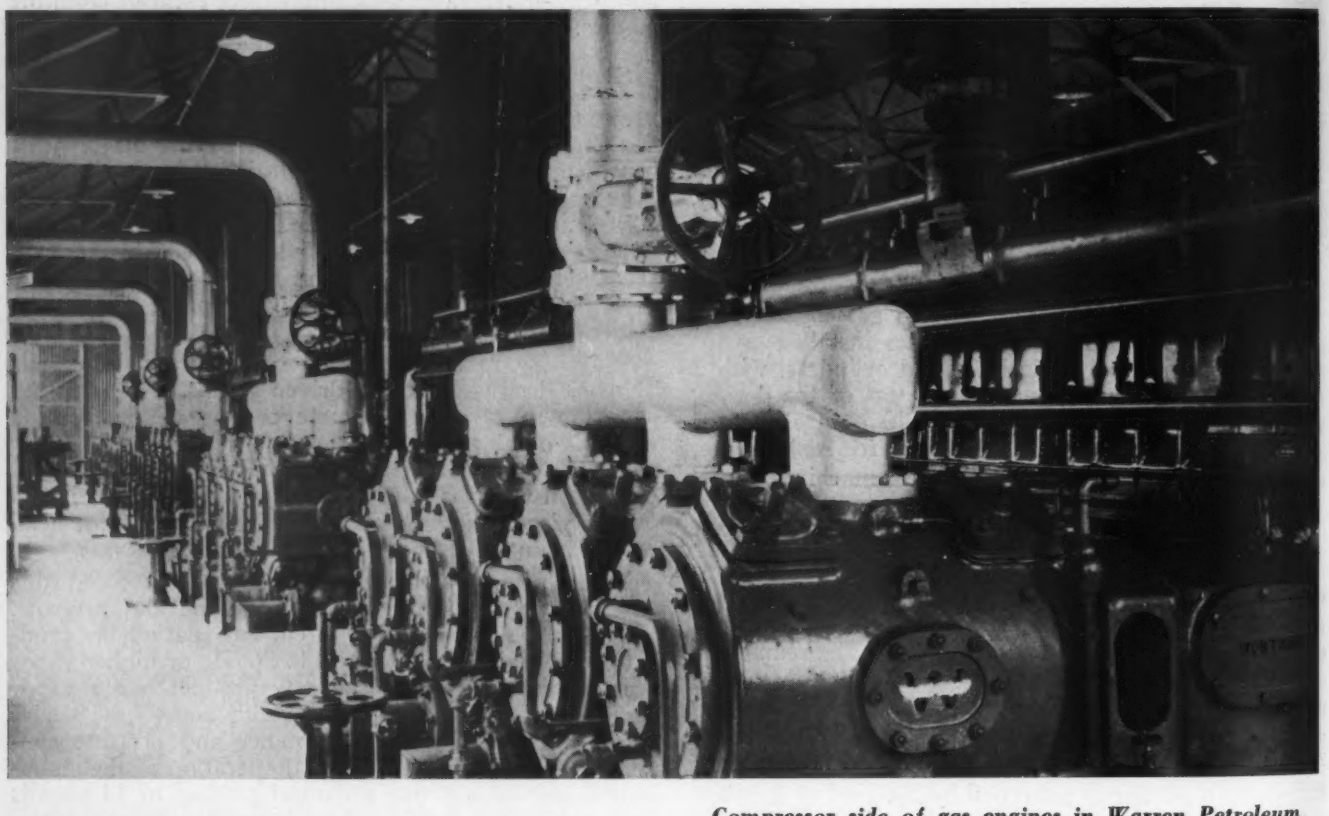
With the exception of the reflux pumps in the building which houses the fractionating and condensing equipment, all circulation of oil, gasoline, and water is obtained by electric motor drives. In order to make this possible, the company included generators in the design of the plant which are driven by 165 horsepower vertical gas engines. The three units when operated to their rated capacity generate 375 k.w., which is sufficient to furnish lighting for the various units in the plant and to operate the deep well pumps, in addition to the water circulating pumps, the rich and lean oil pumps, and the loading out pump.

The two oil pumps and the gasoline pump are located outside the main building and have weather-proof motors which do not require protection from the elements. Gasoline is loaded in tank cars on a switch about one-half mile distant with a four-inch line used. Under certain conditions, tank cars have been loaded from plant storage at the rate of one car each 23 minutes. sufficient pressure is always held upon storage so that the pump is taking suction under pressure to prevent gassing of the impeller case.

Storage for the usual grade of natural gasoline was placed by installing horizontal pressure vessels, and for butane, underground tanks. The butane tanks are 150 feet long, in pairs, made in the factory in sections and welded on location to form the long tanks. They were set three feet below the ground surface in order to obtain the full benefit of soil insulation to maintain low temperatures while holding the liquid in storage. A building was placed over one end of these vessels with a concrete lined pit, which contains the exposed ends of the tanks to show the liquid level through gauge glasses. In addition to the usual type of pressure storage vessels for stabilized natural, two 10,000-barrel tanks were installed with flat pan roofs, which are for use when storing low vapor pressure gasoline. The construction of the roof on these tanks will permit circulation of water during the summer months to lower the temperature of the vapor space below the roofs.

Pumps will be used to circulate water over the tops of these tanks, taking water from the louvre tower basins which will travel through a pipe line system to and from the tops of the tanks. As the highest temperature in this region is encountered during July, August, and September, and then only during the afternoon, the job of circulating water for vapor space cooling will be intermittent.

At present, both butane and propane are manufactured from a single column, but a third tower is being erected to handle butane fractionator tops so that continuous operation can be obtained and bottom products from both towers finished to specifications. Provisions are made to carry the butane stabilizer overhead condensate to mineral seal after-coolers so that the temperature can be lowered sufficiently that a less amount of oil will be necessary than with standard practice, to absorb all the desirable fractions from the gas. As after-chilling of the absorption oil will only be neces-



Compressor side of gas engines in Warren Petroleum Company's Galva gasoline plant.

Back side of five of the ten eight-cylinder gas engines.

sary during the hottest months of the year, compressors used during the winter to boost residue gas into the transmission lines of the gas company can be used to handle the extra volume of propane vapors needed to obtain lower temperatures on the oil without the installation of additional machinery.

CONTINUOUS OPERATION

With the new column in operation any blend of butane and propane can be manufactured continuously which will meet the approval of drilling contractors who use this type of liquified petroleum products instead of gas or gasoline when drilling wells in isolated communities or districts. Numerous rigs are being operated in the Russell County pools for drilling, as natural gas is not produced with the oil from many wells in that part of Kansas.

The stabilized natural, regardless of the vapor pressure, is removed from the lower section of the stabilizer in the usual manner and transferred to a working tank near the treater. From this vessel, the gasoline passes continuously to the vessel containing the copper sweetening material. Between the work tank and the treating vessel, a manifold is installed which contains two manometers which are used to regulate the flow of gasoline and air. An orifice installed in the gasoline line indicates, through the manometer, the flow of gasoline, and a smaller orifice in the air line indicates the drop in pressure across it while the air is flowing to the treating vessel.

Two-inch lines are used to carry the gasoline from the work tank to the treating vessel. It is fitted with stops for controlling the flow, and with a mixing device at the point of contact with the air under pressure. The mixing device is equipped with a tangential nozzle to give the gasoline a swirling effect, while the air enters directly at the base of the mixer and flows upward into the liquid. Under certain conditions, a pressure of 34 pounds is used on the treater, with a 1-inch differential of air across a ⅛-inch orifice. The mixture of air and gasoline enters the base of the treating vessel contianing the copper compound, below a retaining mat of steel wool upon which the solidified treating compound rests. Approximately 18 inches of this mat is used in this size treater, with a manhole in the side of the vessel for arranging the support or removing it when necessary.

It has been stated that the reaction of the mercaptans in the gasoline with the copper treating solution is esentially the oxidation of the mercaptans to the corresponding disulfides and the reduction of the cupric ion to the cuprous state. Cuprous chloride formed in the reaction is soluble in a solution containing high concentration of chloride salts. The hydrochloric acid evolved by the reactions is also retained in the solution and is said to be essential to the process because cuprous chloride and the hydrochloric acid are reconverted to cupric chloride by oxidation with the air introduced into the gasoline stream before the mixture enters the treating tank.

While the gasoline produced by Warren Petroleum Company at Galva is naturally non-corrosive, it is somewhat sour to doctor. It has been continuously treated in this vessel and with the original charge of solution since the plant was started up July 1936. It has been stated that with this solidified compound of copper salts, if the bed becomes dry from lack of water, the efficiency is lowered immediately, and if too wet, it also fails to function properly. By checking the solution with standard tests provided, this condition may easily be determined, and if too dry, a small amount of steam may be admitted with the gasoline until the required amount of moisture is present.

The treating unit was installed when the plant was first built, with all of the stabilized natural being passed continuously through as it was manufactured, and has continued to produce doctor-sweet and non-corrosive gasoline without additions or subtraction of the compound in the vessel.

Study of Standard Flanged Joints for Piping

CARL L. SIEGEL

EQUAL results should not be expected for the various sizes of flanged joints, even though the flanges are rated in the same working pressure classification. For the flanged joints specified in the American Standards Bulletin, A.S.A. B-16e, in the 150 and 300 pounds W.P. classification, some sizes provide a better designed joint than others, when the customary raised facing is used. While it is not to be expected that each joint should be exactly the same in design, the actual variation is large enough to warrant consideration in the erection of piping.

The A.S.M.E Code for Unfired Pressure Vessels provides rules for the design of flanged joints. It also states that the dimensions of flanged joints given in the A.S.A. classifications for the various working pressures, such as 150 and 300 pounds, are acceptable for the piping connections to pressure vessels. However, sizes of connections other than the standard pipe sizes must be designed according to the recommended rules. An application of these rules to the flanged joints of standard pipe sizes discloses varying results.

The code procedure for the calculation of flanged joints states that the total allowable bolt load must equal the sum of the end thrust due to the internal pressure and the total gasket pressure. This may be expressed as:

$W = H + G$

W = total allowable bolt load, lbs.
H = hydrostatic end thrust, lbs.
G = total pressure on the gasket, lbs.

The total load applied by the bolts, in a flanged joint, varies considerably in actual practice, depending upon the methods used by the pipe fitters in tightening the joint. Under the code rules, the allowable load for each bolt is set by the allowable working stress. As an example, the allowable working stress for alloy steel bolts, at a working temperature of 700°F., is 14,200 pounds per square inch. This stress is also to be calculated at the minimum section of the bolt, generally the area at the root of the thread. For a standard 1-inch diameter bolt, the minimum section is 0.550 square inch, which with an allowable stress of 14,200 pounds per square inch, gives an allowable load of 7810 pounds per bolt.

In actual practice, the tightening of the nuts by various workmen produces greater bolt loads. Experiments by Kimball & Barr indicate that the actual bolt load is approximated by the figure of 16,000 pounds bolt pull per nominal inch of diameter.[1] For a 1-inch diameter bolt, the bolt loading is then 16,000 pounds which is more than twice the load determined by using the allowable stress, and sets up a unit stress of 29,100 pounds per square inch at the minimum bolt section. Evidently in flanged joints, a greater bolt load is actually established than that determined by the allowable stress given in the code.

The hydrostatic end thrust due to the internal working pressure, as suggested by the code, is calculated by considering the working pressure acting on the area bounded by the outside diameter of the contact surfaces. The figure obtained in this way is probably greater than the actual force occurring from the internal pressure. If the full working pressure is experienced at the outer edge of the gasket, or contact surfaces, the joint will leak. Actually the end thrust may be more accurately estimated by adding to the force obtained by the internal pressure acting on the area bounded by the inside diameter of the contacting surfaces, the force obtained by some average pressure, which is less than the internal pressure, acting on the gasket or contact area. This may be illustrated by assuming that at the inner edge of the gasket the pressure is the internal working pressure, while at the outer edge the pressure must be zero or the joint would leak. The magnitude of the pressure, due to the internal pressure, acting on the contact area will be one half of the internal working pressure if a straight line assumption is made of the pressure decrease across the width of the gasket.

In order to effectively seal a flanged joint, it is considered necessary to compress the gasket between the flanges. The gasket being of a softer material than the flanges is deformed to fill out any unevenness occurring between the flanges. To insure that the gasket is deformed, sufficient pressure must be applied by the bolts. The unit pressure on the gasket is generally given as some multiple of the internal working pressure. The ratio of the unit gasket pressure to the internal working pressure is called the contact-pressure ratio. A correct value for the contact-pressure ratio depends upon the type of flanged joint, the method of facing the flanges and the gasket material. It is also a factor which may apparently be assigned a wide range of values. For raised face joints, values of 10 to 12 are given for the contact-pressure ratio by some gasket manufacturers. Walker and Crocker[1] state that the compression in the gasket, before applying the internal pressure, is generally 8 to 12 times the internal working pressure. After the internal pressure is applied, the contact-pressure ratio should be from 4 to 8. Here, in itself, is a fairly wide range of variation and there is little information to aid in a correct selection of the value to use in the design of a joint.

Applying the procedure, suggested in the A.S.M.E. Code, to flanged joints in the standard 150-pound classification, the results given in Table 1 show the variation of the contact-pressure ratio with the nominal pipe size. These figures were based on a rated

working pressure, for all sizes, of 150 pounds per square inch at a temperature of 500°F. Bolts were considered of alloy material having an allowable working stress of 14,200 pounds per square inch at the above temperature.

TABLE 1

Pipe Size, Inches	Contact-Pressure Ratio	Pipe Size Inches	Contact-Pressure Ratio
2	9.24	10	7.12
2½	7.48	12	4.71
3	4.54	14	6.00
3½	9.17	16	6.55
4	7.05	18	6.25
5	8.34	20	7.20
6	6.04	24	7.00
8	3.64	..	....

The values for the contact-pressure ratio show a variation of from 9.24 to 3.64. Now, if a contact-pressure ratio of 9.00 is considered to be conservatively safe for the design of joints then 3.64 is too low a figure for the design of a joint in the same pressure classification. The flanged joints of 2 and 3½-inch pipe are the best joints and present the least hazard of showing leaks in service. By the same reasoning, based on contact-pressure ratios, the joints for 8 and 12-inch pipe are the worst of the group and require more care in erection to provide tight joints at the flanges.

If a certain value of contact-pressure ratio is assumed, the actual allowable working pressure as determined by the flanged joint design, varies for the different pipe sizes. The figures given in Table 2 show the allowable working pressures, when a contact-pressure ratio of 9.00 is used for all joints listed in the 150-pound classification. As before, the maximum working temperature is 500°F., and the allowable stress in the bolts is 14,200 pounds per square inch.

TABLE 2

Pipe Size, Inches	W. P. Lbs./Sq. In.	Pipe Size Inches	W. P. Lbs./Sq. In.
2	154	10	126
2½	129	12	94
3	87	14	113
3½	152	16	120
4	123	18	116
5	142	20	128
6	110	24	126
8	79	..	...

Consideration of these figures, indicate that in the majority of sizes, the design is not suitable for the rated 150 pounds per square inch working pressure. While some sizes come close enough to the rated working pressure that their ability to withstand the service may be conceded, others show values too low to promote confidence in their serviceability.

The same wide variation may be observed in the standard classification for 300 pounds per square inch working pressure. Basing calculations on a rated working pressure of 300 pounds per square inch for all sizes, at 750°F., and an allowable stress in the alloy steel bolts of 12,600 pounds per square inch, the values for the contact-pressure ratios are given in Table 3.

The variation of contact-pressure ratio for this classification, ranges from 10.40 to 2.65. This shows a greater variation than was obtained for the 150-pound flanged joints and also shows a generally lower average value for the contact-pressure ratio throughout the group. Joints in 2½-inch pipe should

TABLE 3

Pipe Size, Inches	Contact-Pressure Ratio	Pipe Size, Inches	Contact-Pressure Ratio
2	8.00	10	4.93
2½	10.40	12	4.57
3	6.50	14	5.40
3½	5.50	16	5.60
4	4.06	18	4.63
5	2.65	20	3.67
6	3.33	24	4.30
8	3.19	..	...

give the least trouble, while those in 5-inch lines evidently require careful attention to their assembly.

By setting up the value of 9.0 for the contact-pressure ratio and using an allowable bolt stress of 12,600 pounds per square inch, at 750° F., the values obtained for the allowable working pressures of the 300-pound standard flanged joints are given in Table 4.

TABLE 4

Pipe Size, Inches	W. P. Lbs./ Sq. In.	Pipe Size, Inches	W. P. Lbs./ Sq. In.
2	272	10	195
2½	340	12	187
3	229	14	210
3½	201	16	216
4	162	18	190
5	126	20	169
6	146	24	187
8	146	..	...

By this method of calculation most of the flanged joints in the 300-pound standard classification apparently fall short of being well designed for their rated working pressure. From the values of allowable working pressures obtained, the inclination would be to assign a more conservative value than 300 pounds per square inch as the actual working pressure, in service, for this group of flanged joints.

To offset this apparent inconsistency in flanged joint design, actual service has proven the ability for satisfactory service for all sizes of pipe in both the 150- and 300-pound classifications for flanged joints. The answer to this possibly lies in the fact that in actual service the bolts are stressed to a far greater extent than the allowable working stresses named by the A.S.M.E. code. A greater bolt pull would increase the pressure on the gasket and reduce the possibility of leakage at the joints. The bolts may, however, be stressed to such a point that a reasonable factor of safety is no longer in effect. By using the method of determining the actual bolt pull, as suggested by Kimball and Barr, and a working pressure of 150 pounds per square inch for all sizes, the values for the probable contact-pressure ratios are shown in Table 5 for flanged joints of the 150-pound standard classification.

TABLE 5

Pipe Size, Inches	Contact-Pressure Ratio	Pipe Size, Inches	Contact-Pressure Ratio
2	35.7	10	20.2
2½	30.0	12	14.8
3	19.7	14	15.4
3½	36.0	16	16.7
4	28.8	18	14.0
5	26.8	20	15.9
6	20.5	24	13.2
8	14.4	..	...

Values for the probable actual contact-pressure ratio obtained in flanged joints for the standard 300 pounds per square inch classification are shown in Table 6.

[*Continued on page 435*]

Cracked Gas Oils *for* Diesel Fuels

HAROLD BOTTOMLEY

CONSIDERABLE literature has been published regarding Diesel fuels, their sources, specifications, qualities desired, etc. It is generally conceded that in the high speed engines fuels of predominately paraffinic nature or those of high cetane number should be used. Considerable experimental and practical knowledge confirm this contention.

With the increasing premium placed on virgin stocks for cracking purposes it has become more and more evident that some compromise must be effected as regards the Diesel fuels of the future. Modification of engine design or addition of "dopes" to the fuel are likely alternatives. Naturally much depends on the rate of public acceptance of the Diesel engine. It seems that there are definite applications for each type and that neither will be entirely displaced. Diesel fuel production by hydrogenation of carbonaceous materials may be an industry of the future. Many speculative opinions may be voiced and some must be given credence.

The classification of Diesel fuels for low-, medium- and high-speed engines is vague as may be seen by comparing various engine manufacturers' recommendations. Each manufacturer apparently knows the type or types of fuel that will perform most satisfactorily in his engines, but these same fuels may behave atrociously in another make of engine of the same speed rating. Much depends on the type of injection system, style of combustion chamber, and other factors.

Be all this as it may, the refiner or marketer of Diesel fuels is solely interested in supplying the fuel of the desired characteristics with a minimum of difficulty and a maximum of profit. To attain this important end it is imperative that a fuel made from the cracking process or a blend of this fuel and straight run material or a fuel "doped" to meet requirements, be supplied. It is more or less general knowledge among refiners that cracked gas oil can be used very effectively in certain types of Diesel engines. Rather than attempt to market Diesel fuels unsuitable for satisfactory operation, the following investigation was made. It is by no means conclusive but may give some information not at present available elsewhere.

The tests were run on a Fairbanks-Morse, 2-stroke cycle, 12 by 15-inch vertical, single cylinder, solid-injection type engine. The full load speed was 300 RPM and the brake horsepower delivered in all the tests was forty. Four different fuels were used with properties as given in Table I. All were fully distilled overhead products and ranged in API gravity from 13.6 to 32.2. The Saybolt Universal viscosities at 100°F. ranged from 36 seconds to 108 seconds. No deductions can be made from these tests regarding the proper viscosity for use due to the short duration of the tests. This statement has special reference to lubrication of fuel injection pumps, cylinder walls and piston rings.

Fuel No. 1 was a virgin gas oil and fuels 2, 3, and 4 cracked gas oils of various degree. Fuel No. 1 started easily and caused only normal color in the exhaust. No detonation or erratic operation was noted when using this fuel.

Fuel No. 2 performed almost as satisfactorily as Fuel No. 1 with the exception of a slightly darker exhaust and a very little pound. No. 3 fuel performed intermediately between Nos. 1 and 2 if such a close distinction is possible. No. 4 fuel gave considerable trouble when starting, exhaust was dark and engine pound was very marked. Loping of the engine under no load was very noticeable. When full load was applied the loping diminished but the detonation continued in moderate intensity. Altogether, this fuel would probably be condemned as not being

TABLE 1

Fuel No.	1	2	3	4
Kind of fuel	Virgin Gas Oil	Crude Gas Oil	Crude Gas Oil	Heavy Recycle Gas Oil
Gravity ° A.P.I.	32.2	20.4	28.0	13.6
Aniline number	154	117	103	110
S.U. at 100° F.	42	55	36	108
*Diesel Index	49.6	23.9	28.8	15.0
*Cetane Number approximate	60	40	45	35
Characterization factor, K	11.6	11.0	11.1	10.7
Average boiling point	570	620	490	690
*Percent hydrogen	12.5	11.1	11.4	10.2

* Calculated values.

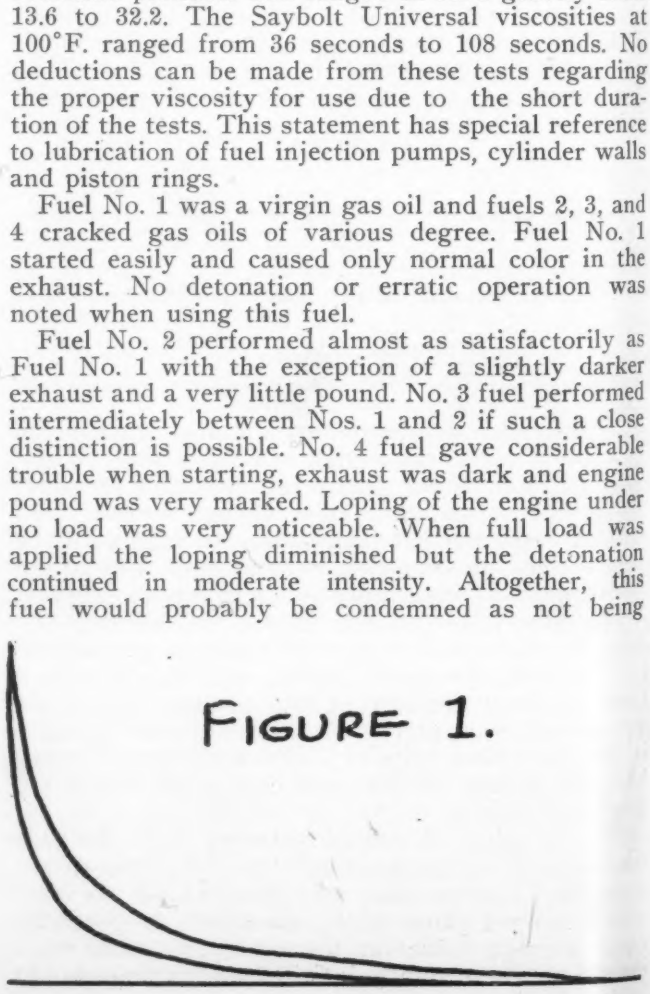


FIGURE 1.

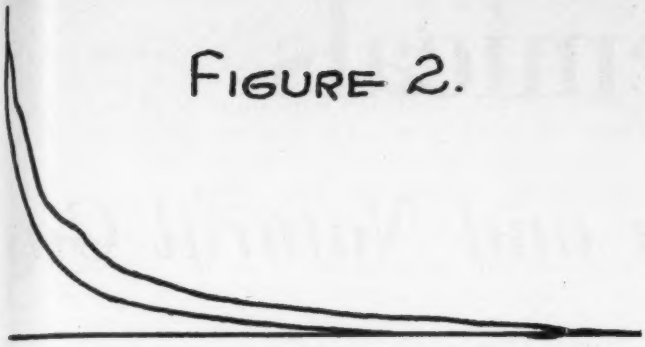


FIGURE 2.

adequate for satisfactory operation of even slow-speed engines.

In Table II is tabulated some data taken during the tests and from it some interesting deductions may be made. Probably the most interesting items are ignition and maximum pressures attained in the engine cylinder. These were taken from five indicator cards taken on each fuel and respectively averaged. Figures 1, 2, 3, and 4 are actual indicator cards taken on the test engine when operating with the respective fuels. These clearly indicate the source of much of the following discussion. It will be noted that the data are in line with expected results.

With the most paraffinic fuel the ignition pressure was 394 pounds per square inch, and the maximum pressure attained at constant volume is 627 pounds per square inch. Combustion was normal with this fuel and the expansion or power stroke curve shows this fact plainly.

Fuel No. 2 did not ignite until a pressure of 405 pounds per square inch was reached but the abrupt pressure rise only attained a maximum of 626 pounds per square inch. Combustion was a trifle erratic as may be seen from the wavy expansion curve, each little plateau denoting a short period of delayed burning of the fuel. No erratic operation was noted in engine under test.

Fuel No. 3 ignited at a temperature corresponding to a pressure of 408 psi slightly higher than that of No. 2. This may probably be explained by the fact that the molal average boiling point of fuel 3 is lower than fuel No. 2 thus requiring a higher kindling temperature. The maximum pressure attained in the cylinder while using fuel No. 3 is considerably higher than those of fuels 1 and 2. After developing a pressure of 647 pounds per square inch the fuel burned smoothly to the exhaust position.

Using fuel No. 4 ignition was effected at a moderate pressure of 408 pounds per square inch but instantaneously the pressure rose to 679 pounds per

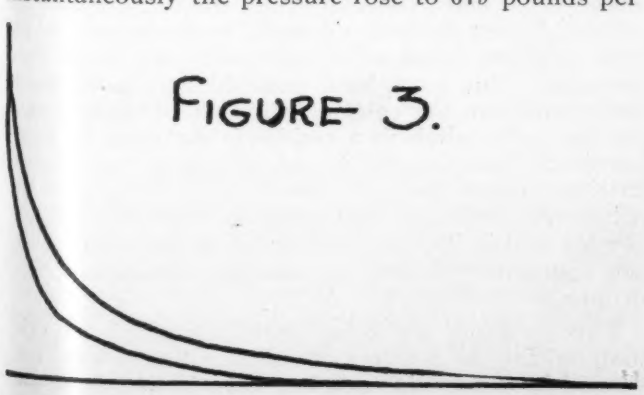


FIGURE 3.

TABLE 2

Fuel No.	1	2	3	4
Fuel used, lbs./BHPH	.47	.51	.51	.549
Horsepower developed	40	40	40	40
Fuel per hour, gallons	2.61	2.63	2.77	2.70
Ignition pressure, psi	394	405	408	406
Maximum pressure, psi	627	626	647	679

square inch, the highest caused by any of the fuels. As ignition took place a decided pound was apparent. Uneven burning of the charge is shown by the decidedly wavy line on the power stroke.

Measured in pounds per brake-horsepower-hour fuel consumption, it will be noted, is less for the straight-run fuel and highest for the most highly cracked stock. This is as would be expected, but it will be noted that with fuel No. 2 practically the same number of gallons of fuel per hour is consumed. Since gas oil is sold by the gallon, the latter figure is the one on which to base cost comparisons.

The consumption of fuel No. 3, based on pounds per BHPH, is the same as fuel No. 2, but due to higher gravity the number of gallons consumed is slightly more. With fuel No. 4 the rate per BHPH in pounds is highest, but due to the low gravity the gallons per BHPH is close to the others.

On considering the above four oils as to performance, No. 4 is immediately rejected as being unsatisfactory, both from a starting and running standpoint. The other three oils are very satisfactory as

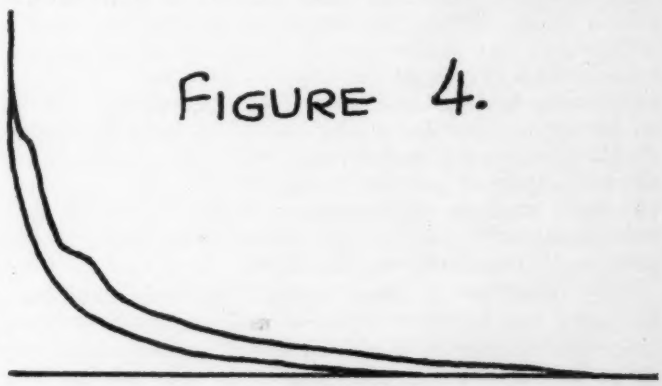


FIGURE 4.

regards performance, but if a price comparison is made, No. 1 oil is at a disadvantage due to the premium that is held on it. Very seldom does a quotation on virgin gas oil appear in the trade journals, and when it does it is usually under the name of "Diesel-fuel." Its price as such is usually one-half to three-quarters of a cent higher per gallon than "zero" cracked gas oils.

The writer does not contend that all Diesels will satisfactorily operate on all cracked gas oils, but he does maintain that most Diesels will do so. In view of the widely divergent Diesel fuel specifications advocated by various engine manufacturers it is certainly a fact that many Diesel operators are not operating their engines on the most satisfactory and economical fuels at present available.

The writer advocates that Diesel operators investigate their fuels and the possibilities of improving the types for them. It is possible that considerable saving may be effected by those that are able to replace their straight-run gas oil fuels by cracked products. For example, a plant operating 1000 HP of Diesels will save in the neighborhood of $3000 per year by so doing.

Organic Chemicals

From Petroleum and Natural Gas

M. B. COOKE, C. R. WAGNER and H. R. SWANSON

Presented before the Second World Petroleum Congress, Paris, France

ORGANIC Chemicals From Petroleum and Natural Gas is a subject in which relatively few persons have been seriously interested. As to the future, it is believed that, instead of a relatively few people being interested in this subject, millions upon millions of people will be affected in one way or another by the chemicals from petroleum and natural gas which will certainly appear in our future commerce and will be associated with our daily living.

SCOPE OF PAPER

With such a broad subject it becomes necessary to confine ourselves to those products which are already being made from petroleum and natural gas which are of sufficient interest to attract the attention of both scientists and capital, a partnership which is absolutely fundamental to the successful solution of the numerous problems involved in the exploitation of the possibilities of the raw materials, petroleum and natural gas. The organic chemicals so far made from these raw materials have been the result of applying well known aliphatic chemistry to the utilization of the raw materials. It is also apropos to credit modern engineering and its alloy steel development with part of the success which this comparatively new industry has had.

The question is often asked why this chemical industry has been so slow in making itself known since the chemistry involved has long been known? A proper answer is difficult, in a few words, but the essence of the situation is that the investigative work required large sums of money, the collateral for which was of questionable value due to the impossibility of predicting the fruits of research on a given date. Predicting the mass production of shoes, shovels, and loaves of bread is easy, but the degree of success of commercial research on chemical processes and problems is never known until finished.

HISTORICAL DEVELOPMENT OF MANUFACTURE OF ORGANIC CHEMICAL PRODUCTS

(1) *Coal-Tar as Raw Material*

As an example, we may select the synthetic dye business, which was developed to very large proportions in less than 50 years after Sir William Henry Perkin, in England, discovered the first coal-tar dye, mauve. The basis for this industry was, as its name implies, coal-tar and coal-oils. Comprehensive research of a highly scientific character preceded this commercial development of the dye and chemical field. The reason the coal-tar chemical industry grew so rapidly is that the basic chemical raw materials found in coal-tar were easily separated one from another, which allowed the chemical and physical properties of the individual hydrocarbons to be readily studied. In addition, the hydrocarbons found in coal-tar are very few in number and they happen to be ones that are reactive to the ordinary reagents. As a result, the chemistry of coal-tar and its products grew with great rapidity. In less than a half century after Perkin's discovery of mauve, a well known lexicon listed the properties of over three quarters of a million separate organic chemical compounds, the raw material for which was coal-tar.

(2) *Petroleum and Natural Gas as Raw Material*

Why then have we not built up a huge chemical industry based upon petroleum and natural gas as raw material? The answer usually given relates to the complexity of the hydrocarbons present. This is true to a degree; the petroleum hydrocarbons are complex and little has been known about their reactions with reagents due to the difficulties encountered in separating individual hydrocarbons. This is not the only reason, however, for our failure to develop an organic chemical industry based on petroleum. One of the major causes for delay has been the very great variation between the numerous crude oils from different parts of the world.

By analyzing the problem further, we come to the conclusion that we have not paid enough attention to this very fundamental point: "What causes one coal-tar to be like any other coal-tar and why are crude petroleums not like each other?" We know now that coal-tars are alike because they are the result of man's "controlled" application of heat energy to the mother substance, "coal." Petroleum, on the other hand, is a product of Nature's "laboratories," each crude petroleum differing from the other in chemical constituents, minerals, temperature, time and pressure. As proof of our point, we know that benzene, toluene, xylene, naphthalene, anthracene and phenol are the chief constituents of coal-tar distillates (with pitch as a residue), but none of these materials exist as such in coal. We have been unable to either detect them or remove them from coal by solvents at ordinary temperatures. The most we can say for coal in its raw state, so far as its constituents are concerned, is that it contains carbon and hydrogen.

The aromatics and other chemicals which are raw material for the coal tar chemical industry were not formed by Nature in coal, but were formed from the

carbon-hydrogen material of the coal, by heat energy —by pyrolysis and polymerization.

If we look at the problem in this manner, it appears logical to criticise ourselves for attempting for so many years to build up a chemical industry from petroleum and natural gas as a raw material by worrying about the "complexity of hydrocarbon compounds in petroleum," "the difficulty of separating one from the other," etc.

We should have treated petroleum and natural gas as we did coal, as a raw material, and not as a direct source of individual chemical compounds. We heated coal, energized it and took the products of this heat treatment as our raw material for the coal-tar chemical industry. This was the logical way and paid handsome dividends.

From this analytical "grist" we can readily see that pyrolysis and polymerization were the two main tools by which coal yielded suitable hydrocarbon constituents which were in suitable form to react with chemical reagents at our command and give us the desired organic chemical compounds. Coal, in its raw state, would have yielded none. When we turned our attention to petroleum and natural gas we did not seem willing to use the same tools as we had used on coal. We assumed that because we had a liquid, we did not have to heat energize our new raw material. It now develops that as soon as we turned to first heating our raw materials and then performing our separating steps, followed by recombination of the desired constituents, we have made rapid strides in building the foundation for a new and greater organic chemical industry.

ORGANIC CHEMICALS FROM COAL AND COAL-TAR

When we look back and see that the science of organic chemistry dates from only 1830, and compare this with the progress already made, we have reason with comparative safety to predict many new and novel chemicals and industries. It is quite appropriate that such subjects are being discussed in this city, representing France, since it was Lavoisier who first showed that organic compounds consisted of carbon and hydrogen, and frequently oxygen, to which another brilliant citizen of France, Berthelot, afterwards added nitrogen. Although an Englishman, Scheele, as far back as 1776, had obtained oxalic acid from nitric acid and sugar, and in 1826 Hennel, an English apothecary, had synthesized alcohol, new life was injected into the subject of organic chemistry by the appearance in 1832 of the classical research of Liebig and Wohler on "The Radical of Benzoic Acid," which, they truly said, "might shed a new light on the vast and unexplored region of organic nature."[1] This work was followed by Kekule's discovery of the laws which underlie the structure of organic compounds in 1859. The other cause for the extraordinary development of the organic chemical industry was the industrial application of these discoveries by Perkin in 1856, with his synthetic dye, mauve.

DYES AND EXPLOSIVES

It is apparent that the organic chemical development took place first in the aromatic branch of the great hydrocarbon family. As has been pointed out, coal-tar contained relatively few substances, easily separated from one another, whereas the aliphatic division contained many compounds which are difficult to separate and use as the starting point of a synthesis.

The extent of the industrial as well as the technical development of the dye and drug industry, using for their raw material, oils from coal is too well known to repeat and discuss here. The methods of obtaining the various useful commodities are of interest since our petroleum technologists have borrowed most liberally from their predecessors, in the coal-tar industry. We have, after years of delay, become interested in and have greatly improved the fractionation technique developed by the coal-tar chemists and engineers.

About twenty years ago, the world was engaged in a war, which emergency threw a tremendous load on the technical men of the countries involved. Coal-tar and oils from gas works were found to be insufficient in amount to produce the ever-increasing amounts of aromatics to be used in explosives, drugs, and a hundred other commodities required. Under this stimulus research was hurriedly instituted and it bore fruit even though it was more a technological development than a scientist's program. The tools used by the coal-tar industry, fractional distillation, pyrolysis, sulfonation, nitration, oxidation-reduction, chlorination, hydrolysis, hydrogenation, and compounding, were borrowed and put to work on petroleum as a new raw material. A search for super-aviation fuel was made and one of the best developed was a mixture of benzene and its hydrogenated companion, cyclohexane. Although benzene was fractionated out of selected crude oils, particularly those from Borneo, California, and Russia, the yields were comparatively low.

The demand for toluol for explosives stimulated the search for all aromatics and with the rapidly rising prices for aromatics, huge sums of money were made available for the production of aromatics from petroleum. Hall in England and Rittman in America, and Nobel in Russia sought to increase the yield of aromatics from petroleum by cracking. Large plants were built, under the stress of emergency, and although considerable quantities of aromatics were made from petroleum, no clear cut science was developed nor was a clear conception obtained of the mechanism of aromatic formation from petroleum. It was known that benzene occurred in the product in the ratio of two parts to one part of toluene and xylene. It was also known that the coke oven gases emitted from the coking of bituminous coal contained a higher percentage of toluene and xylene as the temperature of the coking operation was reduced. This meager information was very important to the petroleum chemist in search of aromatics from petroleum because it gave a clue to the mechanism of the reaction.

During the last two years of the war, explosives were made quite successfully from the three main components of an aromatic distillate, benzene, toluene, and xylene. This fact made it less important to take time for studying the reactions involved in order to increase the toluene above the other two aromatics.

The war period created a need for increased yields of aromatics which were used in (1) explosives, (2) solvents, (3) dyes and photographic chemicals, (4) artificial leather coating, (5) lacquer production, (6) pharmaceuticals, and (7) motor fuel. The motor fuel most needed was aviation gasoline of high anti-knock properties and benzene was used in large quantities because of these characteristics. It also was the raw material for the super-aviation gasoline, a mix-

[1] Landenburg's *History of Chemistry*, Edinburgh, 1905.

ture of cyclohexane and benzene called "Hecter," which was used in the Liberty aero engines. From this survey, it is to be noted that the relatively new tool, hydrogenation, was used by the technologists seeking more high grade motor fuel in producing cyclohexane, a hydrogenated benzene. During the post war period, the increased production of aromatics stimulated by the emergency in the war years, led to new problems of outlet for the products. Benzene and other low boiling aromatics were blended with petroleum gasoline and marketed as motor fuel. This outlet for aromatics has continued but the rapidly increasing solvent demands may surpass the motor fuel-blend requirements. The economics involved have gradually reduced the use of aromatics in gasoline.

The use of olefins, from the cracking of petroleum, has received serious consideration only during the past 10 years. Such non-hydrocarbons as ethylene glycol, and isopropyl alcohol, were first introduced on a commercial scale by the Carbine & Carbon Chemicals Corporation and by the Standard Oil Company of New Jersey, respectively.

Synthetic ethyl alcohol from ethylene, has appeared in the past two or three years. Synthetic resins from petroleum gas from cracking stills have appeared in commercial quantities as have also solvents, lacquers, ethers, acetic acid, and acetone.

The future of these industries will depend to a large extent upon the relative prices of raw materials. If the demand for internal combustion motors increases more rapidly than the supply of petroleum and natural gas, other raw materials will be used for these purposes.

ORGANIC CHEMICALS FROM PETROLEUM AND NATURAL GAS BY POLYMERIZATION AND OTHER SYNTHESES

During the past 10 years research on aliphatic hydrocarbon chemistry has received more attention in proportion to the importance of the subject. Such studies have been instituted by governments, universities, and by oil and chemical companies. Years of valuable time were lost in this valuable work but it is particularly gratifying to see the universities' present active interest in this subject. Instead of "cut and try" methods being used to develop new chemical industries and improve the art of refining petroleum and its products, we are now engaged in a more rational program which will not only hasten perfection of new industrial processes but will also be a very powerful force in conservation of natural resources. The Bureau of Mines in the United States deserves honorable mention in this work since it has been a pioneer in the conservation of hydrocarbon resources of all kinds. Of late, the United States Bureau of Standards in cooperation with the American Petroleum Institute has released valuable fundamental data, so necessary to technologists the world over in the development of new industries, in conservation of resources and in the more efficient use of petroleum and natural gas. The work of Rittman and his colleagues on the production of aromatics from petroleum served the United States well. When it is considered that the metallurgy of alloy steels was almost unknown in 1915-1917, the wonder is that Rittman did not have more serious failures of equipment than he did. It was unfortunate that more data were not available at the time on polymerization, the lack of which was one of the serious defects of the processes developed during the war for obtaining coal-tar products from petroleum.

While there are numerous non-hydrocarbon chemicals being made today from petroleum and natural gas, it is our aim to discuss in detail the hydrocarbon products of petroleum and natural gas which are being produced by the two important tools which we have mentioned previously in this paper, (1) pyrolysis and (2) polymerization.

Since pyrolysis must precede polymerization, (in the case of saturated charge stocks), we shall discuss this phase of technology first. As a matter of fact, pyrolysis, or cracking, was used for years, particularly from 1913 to 1927, before much attention was paid to that great class of hydrocarbons, olefins, which were produced as a by-product of the cracking operation. These compounds, particularly those with less than six carbon atoms, have been burned as fuel for years in spite of the fact that their reactions and their chemistry were quite well known. The olefins in the gas from city gas plants have been known, studied, and classified for about 100 years. Michael Faraday, in 1825, obtained some compressed illuminating gas from the Paris gas works; cooled it in a freezing mixture and separated benzene by distillation of the mixture, thus giving a clue to a source of aromatics for future generations.

The utilization of petroleum and natural gas as raw materials for chemicals, particularly the aliphatic chemicals, has not developed as fast as it should have, when it is considered that the olefinic hydrocarbons are very reactive with chemical reagents and even with other hydrocarbons. The reason this utilization has not progressed is well summarized by Brooks[2] as follows:

(1) "Coal has been a cheaper source than petroleum or natural gas for water gas, acetylene through carbide and the benzenoid hydrocarbons. (2) The complexity of petroleum has made difficult the separation of pure raw materials. (3) Until very recently, the magnitude of the developed aliphatic chemical industry has been too small to interest the directors of the oil and gas industry. (4) The necessity for solving problems of the first importance first has left little time and money for ventures into new fields. (5) Perhaps greatest of all retarding factors has been too much orthodoxy, on the part of technical men and executives in regard to the possibility offered by new products and new fields."

The present trend in developing a chemical industry based upon the utilization of petroleum and natural gas is to get away from planning to produce products for markets already developed and being served by industries operating on other raw materials.

Nothing is to be gained for a country in normal times by liquidating successful industries in order to turn out the same products from another raw material even though profits may be greater to certain individual concerns, because in a national emergency, all industries using all kinds of raw material are necessary for success. It appears to be a much sounder plan to attempt to synthesize new products for new uses. This is doubly true when we consider that aromatics have been produced in normal times in sufficient amounts, at a fair price, from coal for several years. It is going backward rather than forward if we develop an aromatic industry simply for the purpose of excluding coal-tar aromatics.

Our known deposits of coal are many times greater than our proved petroleum deposits and to deplete

[2] Chem. & Met. Vol. 44, No. 1, January, 1937, p 18. B. T. Brooks.

unnecessarily our liquid fuel resources is nothing short of criminal. These statements are applicable to countries which have both liquid hydrocarbon resources and solid carbonaceous resources. Economic planning in these countries should look forward to augmenting the supply of aromatics for new uses, the supply for which is not possible by existing normal operations utilizing coal as the raw material. In countries where there is not abundant and, as a consequence, sufficient aromatics are not available, there is available for the first time a new source of aromatics, if petroleum or natural gas is available. Published figures indicate that less than one percent by weight of coal is converted into aromatics by the usual industrial operations whereas there can be produced from seven to ten percent of aromatics from crude oil as a raw material, by pyrolysis and polymerization. It is also of great importance to realize that in the case of petroleum and natural gas operations, as a source of aromatics, there are produced only gases and liquids as by-products. Coal on the other hand produces in excess of 80 percent solid carbon with low percentages of gas and liquids.

Since transportation of the raw material is a considerable item in the cost of the finished chemicals, it is much more economical to transport the raw material which yields several fold more aromatics than other raw materials. It will also be shown later that the by-product gas, resulting from the pyrolysis and polymerization of petroleum contains olefins which are in sufficient quantity to be used as raw material for the production of organic chemicals. The distillation of coal on the other hand, after removal of the aromatics, does not leave by-product gas high in olefin content and particularly suitable as a raw material for the purposes set forth.

The most favorable point for petroleum is probably the fact that all the by-products are liquids and gases, easily transported or converted to other useful products while the 80-90 percent coke by-product of coal is not so readily used or transported.

The first work on polymerization, on semi-commercial and commercial scales was carried on with the view of converting low value by-product gases, resulting from refinery cracking operations to more useful and more valuable motor fuel. The quantities of these gases produced in a year in the United States have been estimated by various technologists and typical figures given by Egloff[3], also by Cooke, Swanson, and Wagner[4]. It is probably safe to assume that from 8 to 10 percent of the crude oil charged to cracking stills, is released as by-product gas. These gases have been studied for their suitability as raw material for chemical manufacture and large plants have been built for these purposes. Due to the very large supply of such gases, however, useful products other than chemicals must be considered if all these gases are to be converted to liquids and solids. Processes developed by Pure Oil Company, Universal Oil Products Company, Phillips Petroleum-Kellogg companies, and by the Anglo-Iranian Oil Company, have been made public and units representing these types have already been installed.

Polymerization comprises the addition of one or more molecules, which may or may not be saturated hydrocarbons, to a molecule of an unsaturated hydrocarbon. As pointed out by Ridgway, Wagner, and Swanson,[5] "It is well to note that an unsaturated hydrocarbon must be present and that the successful operation of a polymerization plant may hinge in some instances, where a rather saturated gas is being processed, upon securing an appreciable conversion of the saturated components to unsaturated hydrocarbons."

Since the largest market for hydrocarbon material is the motor fuel market, it follows that the logical product to produce from refinery gas is polymer gasoline. This has been done on an appreciable scale but the economics involved have seriously hindered the wide scale adoption of polymerization by refiners. A slight shift in the relative market values of petroleum and its products, fuel oil, gasoline, and gas, is all that is necessary to make it highly profitable for refiners everywhere to install polymerization plants for the production of motor fuel—gasoline.

The technology of polymerization, at least by thermal means, has been fairly well developed and the industry may feel confident that a satisfactory technical background exists, to be used in the design and operation of polymerization plants employing the thermal system. Catalytic studies are more complex and more time consuming than thermal studies and for this reason, the petroleum and chemical industries should not expect too much in a short space of time.

The formation of benzene from acetylene by Berthelot by heating the acetylene in an autoclave is probably the first recorded technical information on the possibilities of aromatic synthesis. The reaction is represented by the equation:

$$3C_2H_2 + (\text{Heat}) \rightarrow C_6H_6$$

Sabatier made use of the catalyst, nickel and demonstrated that the reaction takes place at 150°C. (302° F.) and is much safer than heating acetylene without a catalyst. The formation of benzene and other aromatics from petroleum gases is somewhat more obscure and complex but the idea, no doubt, arose from the foregoing study on acetylene. One of the early investigators in this field was a Russian, Nikiforoff[6] who took out a United States patent over a quarter of a century ago for the production of aromatics from the pyrolysis of crude oil.

The Pure Oil Company and Alco Products, Inc., have developed a polymerization process for producing high percentages of aromatics of relatively high purity as compared with the coal-tar distillates containing aromatics. The raw material for aromatic production is either by-product refinery gases or crude oil.

The charging stock for the polymerization unit which is most readily collected is fractionator residue gas, commonly called "stabilizer overhead." The next most convenient source in a modern refinery is absorber residue, commonly called "absorber tail gas." Typical gases from a vapor phase cracking unit are represented by the following analyses:

Composition of Polymerization Unit Feed Stock:

	Mol % Fractionator Residue	Mol % Absorber Residue
CO_2	0.4	0.0
CH_4—H_2	4.9	38.8
C_2H_4	7.9	25.5
C_2H_6	14.5	13.8
C_3H_6	23.0	16.8
C_3H_8	22.2	3.1
C_4H_8	17.7	2.0
C_4H_{10}	9.7	0.8
C_5 plus	0.2	—

[3] Egloff, Gustav, *National Petroleum News*, Nov. 20, 1935, pp. 25, 65.
[4] Cooke, Swanson, and Wagner, *National Petroleum News*, Nov. 20, 1935, p. 33.
[5] Ridgway, Wagner, and Swanson, *National Petroleum News*, Nov. 4, 1936, p. 47.
[6] Nikiforoff, U. S. Patent No. 755,309.

Composition of Polymerization Unit Feed Stock:

	Mol % Fractionator Residue	Mol % Absorber Residue
Unsaturates	48.1	44.3
Spec. Grav. (Air = 1)	1.518	0.993

PURE OIL PROCESS FOR AROMATICS

The development work on this process was carried on with the normally gaseous hydrocarbons with C_4 as the heaviest constituent. Since there is a very great interest in the subject of aromatics from petroleum as well as from such gases, the process utilizing gas oil as charging stock for the pyrolysis step is described. The plant to be discussed was designed to process 300 metric tons of gas oil per stream day, and recovers about 30 percent by weight of aromatic distillate (Figure 1). This distillate contains approximately 24 weight percent boiling within the temperature range 215°-240° F., representing 7.2 weight percent of the original charge or approximately 6500 tons per year based on 300 operating days.

APPROXIMATE OPERATING CONDITIONS

Capacity and Charge:

The plant processes 300 metric tons per stream day of uncracked gas oil, having the following characteristics:

Source	Mixed Base Crude
Gravity, A.P.I.	34
Gravity, Specific	.885
Sulphur, Maximum	.1
Paraffinicity	11.7-11.8
Approximate Boiling Point	
Initial Boiling Point	330—400° F.
10%	440—460° F.
50%	510—530° F.
90%	650—675° F.
End Point, Maximum	700° F.

Yields: Based on processing the above charging stock the estimated yields of products are as follows:

	Weight percent of original charge
Gas	40
Aromatic Distillate	30
Fuel	30
Total	100

The aromatic distillate, by Podbielniak analysis, contains not less than 24 weight percent boiling between 215° and 240° F.

DISTILLATION DATA
(A.S.T.M.)
Aromatic Poly Distillate

Gravity, A.P.I.	31.2
Initial Boiling Point	166° F.
5%	190
10%	195
20%	202
30%	209

DISTILLATION DATA
(A.S.T.M.)
Aromatic Poly Distillate

40%	217
50%	226
60%	239
70%	257
80%	288
90%	336
95%	366
End Point	387
Recovery	99%
Residue	1%
Loss	0
Color, Saybolt	+30

AROMATICS BY PYROLYSIS OF PETROLEUM FOLLOWED BY POLYMERIZATION VERSUS AROMATICS BY CRACKING

The above described process for the production of aromatics from petroleum is more than interesting when we compare it with processes of twenty years ago, such as the Rittman[7] cracking process. Rittman states that Letny[8] heated Baku residues in a 7-foot by 1-inch tube to 700°-800°C., in the presence of charcoal and obtain 40-50 percent tar which yielded 17 percent benzene, 0.4 percent anthracene, and 7 percent naphthalene. This attempt to secure aromatics from petroleum by pyrolysis was probably the first recorded.

Armstrong and Miller[9] reported that their experiments had shown the liquid formed during the decomposition of petroleum gases contained a mixture of the hydrocarbons of the C_nH_{2n}-2 series (olefins). The liquid was rich in benzene and toluene and

[7] Rittman, W. F., et al, manufacture of gasoline, benzene-toluene from petroleum and other hydrocarbons. *U. S. Bureau of Mines* Bull. No. 114, 1916.
[8] Letny, Alexander, *Chem. News*, Vol. 38, 1878, p. 211.
[9] Armstrong, H. E. and Miller, A. K., *Chem. News*, Vol. 51, June 26, 1885, pp. 307-309.

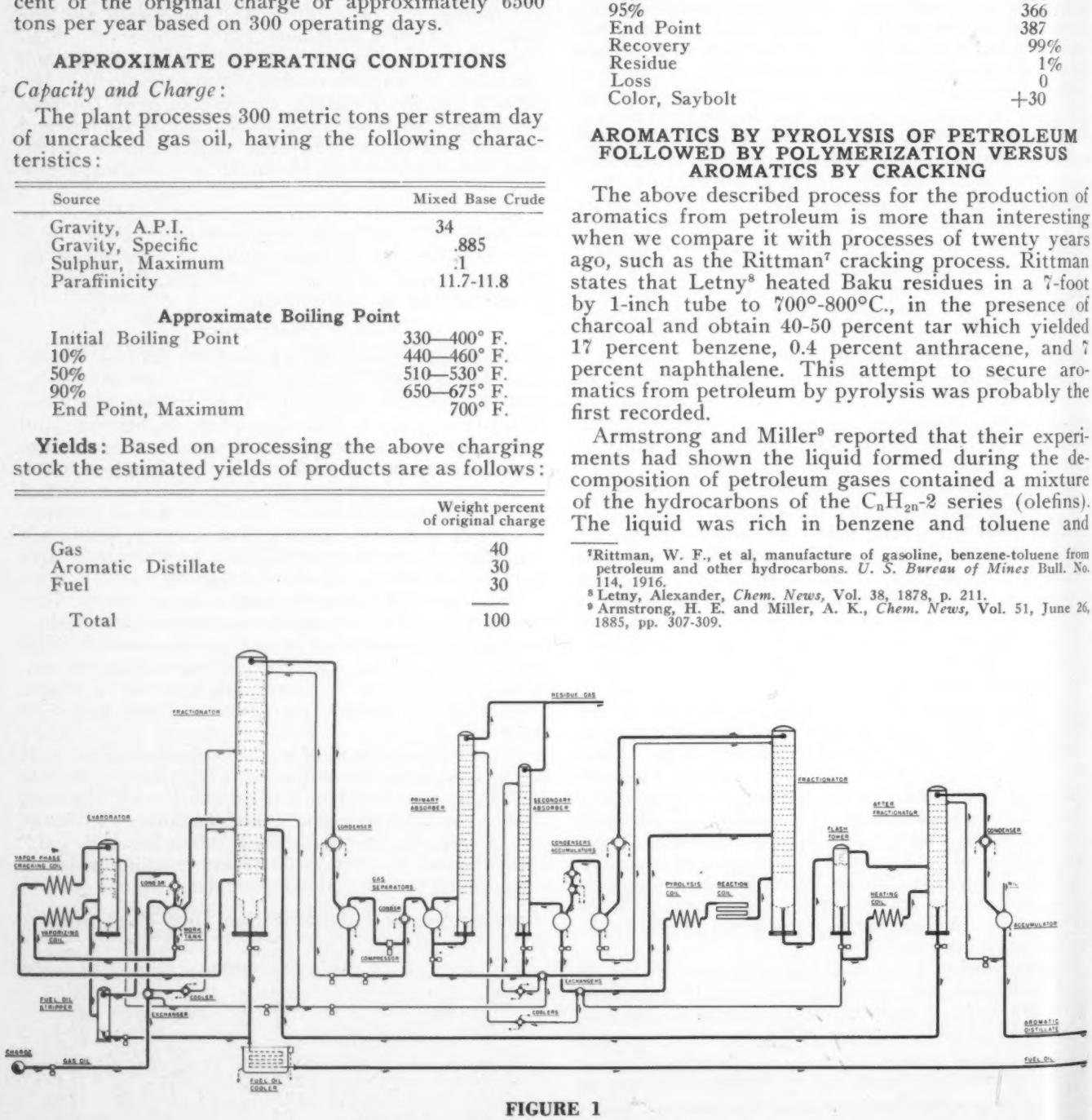


FIGURE 1
Flow diagram Cracking and Polymerization unit.

showed a trace of the higher aromatics. This work, it is believed, is the first published in which the olefinic gases are given credit for being the material from which aromatics are produced and they advanced the theory that the aromatics are not built up from acetylene. From a practical standpoint, however, Nikiforoff (reference cited) appears to be the pioneer in suggesting a two-step process for the manufacture of benzene - toluene from petroleum, the purpose of which was to enable the decomposition to be carried on under two different conditions. He proposed to feed crude oil into a series of decomposition retorts, the course of the liquid being obstructed by baffles so that the heating was prolonged. A temperature of 500-525°C (932-987° F.) was maintained without pressure. The vapors passed through the retorts to a separating tank maintained at a temperature of 200-250°C. (392-482° F.) where the heavier products were condensed. The more volatile products (products boiling below 200°C. (392° F.) which remained uncondensed at that temperature, were then conducted to a separate retort where they were subjected to a temperature of 750-1000°C. (1652-1832° F.) and to a pressure of about two atmospheres (30 pounds per square inch).

DISTINCTION BETWEEN PROCESSES

The prior processes disclosed in the literature were primarily adapted to and dependent on the use of oils that were of a highly favorable character and in connection with which the reaction necessary for benzene-toluene production is comparatively simple. These oils either contained the polycyclic (asphalt) compounds that decompose on simple splitting into benzene and its homologues, or else naphthenes were present, which yield aromatic hydrocarbons through the simplest sort of dehydrogenation. Practically all of these prior processes were operated at atmospheric pressure, indicating the simplicity of the reaction involved, as compared with the production of the low-boiling aromatic compounds from oils in which naphthenes and aromatics do not naturally occur, as accomplished by the Pure Oil process. It was not until 1916 that any literature appeared suggesting the transformation of paraffin hydrocarbons into aromatics. Credit should be given to Prof. Milton C. Whitaker, of Columbia University, for his active cooperation and assistance in the study of oil-gas production and the production of aromatics, for this research work paved the way for later work on pyrolysis and polymerization for the production of aromatics from paraffinic oils. The benzene-toluene process of Rittman's was operated at 625-675°C (1157-1247° F.) and at a pressure up to 250 pounds per square inch. Rittman charged gas oil as raw material but failed to recognize the fact that it was necessary to separate his gaseous products from his liquids and separately treat the gases by polymerization. This omission is not readily understood for Rittman stated that "As regards processes carried out entirely in the gaseous state the temperature can be chosen that is most favorable for the maximum conversion and the minimum of decomposition into undesirable end products, whereas that pressure is employed which experiment has determined to be most favorable in increasing yields and improving the character of the product. In the production of aromatic hydrocarbons it is necessary in a considerable degree both to break down the larger molecules to ethylene or acetylene hydrocarbons and then to polymerize these unsaturated hydrocarbons. Experiment has proven that aromatic hydrocarbons are polymerization products of acetylene and ethylene hydrocarbons as well as the results of the splitting of polycyclic compounds. It thus becomes necessary to employ the high temperatures favorable for olefin and acetylene formation and the high pressure favorable for polymerization. The combination of these two factors results in a higher percentage of carbon formation. Thus it is evident that because of the increase in carbon formation with increase in temperature, it is not commercially desirable to employ the highest temperatures favorable for forming the desired reaction products, but instead to employ a mean temperature that will give a favorable degree of conversion with a reasonable production of carbon. This consideration is of moment only in the manufacture of benzene and toluene."

The process as described in this paper was the first process in which the exothermic nature of the polymerization reaction was taken into account. Previous investigators had attempted to carry on an endothermic reaction, pyrolysis, in the presence of a definitely exothermic one (polymerization). Until this basic principle was applied, no one could have attained the yields, ease of operation, and freedom from coke troubles which are now commonplace with the Pure Oil operation.

Another fundamental innovation to the art of pyrolysis and polymerization has been the direct quenching of reaction products so that accurate control of time of reaction has been made possible. When it is realized that in these reactions we are working with seconds and not minutes of reaction time, then the necessity of direct quenching is appreciated. No indirect cooling device has been developed that will instantaneously reduce the temperature of gaseous-liquid reaction products two hundred to four hundred degrees and still give satisfactory operation.

PURITY OF AROMATIC DISTILLATES

The purity of aromatic distillates is a very important characteristic to be taken into account. It has long been known that aromatic distillates from water-gas tar and distillates from coal-gas differed materially in purity. The coal-tar refiner used fractional distillation as his main tool in separating benzene, toluene, and xylene from these distillates. This problem is easy when certain other hydrocarbons are not present, for instance, paraffins. The presence of olefins offers no difficulties for a simple wash with sulphuric acid removes them. The presence of paraffins, however, offers more serious operating problems. Since water gas results partially from the cracking of petroleum, used to enrich the gas, it follows that a higher percentage of paraffins is found in water gas distillates. In later years this defect has largely been overcome since research has shown how oils can be used in the formation of water gas and recover an aromatic distillate which is rectifiable without difficulty. The reason for fractionation difficulties in separating the individual aromatics is that paraffins are present which either have approximately the same boiling points as the aromatics or form constant boiling mixtures.

The production of aromatics by pyrolysis of petroleum oils or gases, followed by polymerization, at first, was beset with the same problems. Recent work, however, has resulted in the surmounting of the trouble. It has been established that all types of crude oils, from light distillates to heavy residuum, can be made to yield aromatic hydrocarbons in com-

mercial quantities by the Pure Oil pyrolysis-polymerization system. The yield of aromatics will depend upon the relative amounts of vaporizable and crackable oil which each class of oils will yield. Coking troubles have been eliminated and the quality of the aromatic distillates will be uniform regardless of the raw material charged.

PRODUCTION OF OLEFINS FROM CRUDE OIL

From the foregoing development work there has been a great amount of data collected which has led to a new process which serves as a basic one for producing intermediates such as olefins, etc. which will be used by the organic chemical industry. It is well known that cracking-still gases, a by-product of the production of cracked gasoline from crude oil, contain appreciable quantities of olefins; from 15 percent in the case of liquid phase units to 50 percent in the case of vapor phase processes. The use of these gases, especially the lean liquid phase gases as raw material for chemical synthesis is not very practical. The expense of separating methane, ethane, and other saturates is too great at present. The pyrolysis studies carried on in conjunction with polymerization have resulted in the development of commercial processes for pyrolyzing saturated gases as well as gas oil or reduced crude oil to yield gases which are high in olefin content. Separation of ethylene, propylene, butylene, and amylene is now a commercial achievement and plants are already designed and some partially installed (Figure 2).

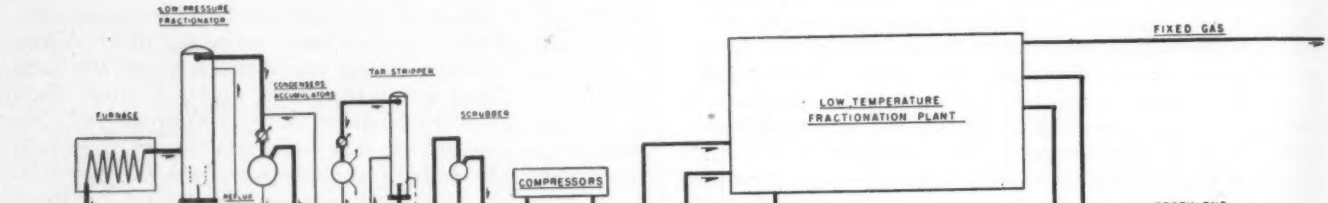


FIGURE 2
Plant for production of Olefines.

Brooks (reference cited) has pointed out that "Until recently equipment designers having experience in gasoline recovery and stabilization have attempted to apply the method of absorption and distillation under pressure to the separation of the two low-boiling hydrocarbons, ethylene, and propylene. However, as is clearly indicated by the vapor pressure curves of these substances at low temperatures, their separation is much easier by the low temperature fractionation of gases rich in them."

Alco Products, Incorporated, has been able to separate about 90 percent of the ethylene from a cracked gas containing from 20 to 30 percent ethylene, as a fraction containing as much as 98 percent ethylene and 2 percent ethane as an impurity.

Ethylene of 90 to 98 percent purity, with ethane as the impurity, will serve without further treatment as ideal raw material to produce by direct synthesis anhydrous ethyl alcohol at a very low cost; ethyl chloride, ethylene chlorohydrine, ethylene dichloride, dibromide, and numerous other ethylene derivatives. The manufacture of glycols for use as antifreeze has been established on a commercial basis for some years now and is receiving a great amount of attention due to the widespread use of the safety explosive, glycol dinitrate. The low freezing point of this explosive is very desirable as well as its unique characteristic of being extremely difficult to detonate except with a heavy cap. This development alone opens up a new field for petroleum for it is no longer necessary to have aromatic coal tars as raw material for modern high velocity explosives. It is also possible to be without coal and petroleum and still make glycol dinitrate since ethyl alcohol will yield about 92 percent ethylene when properly processed. A country with alcohol is made more or less independent of coal-tar and petroleum in regards to high explosives. When petroleum or natural gas is available, however, ethylene can be produced much more economically from them than it can be from alcohol.

A considerable future exists for propylene due to recent discoveries in the field of high octane motor fuel.

Announcement by the Standard Oil Company of New Jersey in 1935 of the unusual properties of isopropyl ether as a high antiknock airplane fuel paved the way for a new industry, in that another by-product of cracking or product of petroleum by pyrolysis is made available as raw material. Isopropyl ether with only 1 cc. per gallon of tetraethyl lead gives a 100 octane fuel which is usable by aviation air cooled motors. Klein[10] has pointed out the advantages of using 100 octane fuel in airplane engines instead of 92 octane fuel. He has shown that an increase of 8 octane numbers, from 92 to 100, has resulted in an increase of 15-30 percent in power output and the speed of the plane was increased from 15-25 percent. The tests made and reported were made with a fuel composed of a very high percentage of iso-octane which is not very susceptible to tetraethyl lead. Isopropyl ether on the other hand is susceptible to lead and for this reason it is of particular interest. The ultimate production of isopropyl ether is many times the possible production of iso-octane unless some new process for the manufacture of the latter is worked out.

Klein (reference cited) brings out the fact that "aromatic fuels, containing no iso-octane may be of decided value in the future since new methods for the economical production of aromatics make it appear certain that considerable more can be produced

[10] Klein, F. D., U. S. Army, *S. A. E. Meeting Paper*, June, 1936.

than was available fifteen years ago." It appears certain that commercial engine manufacturers will design new engines to take advantage of the economics and other desirable features of these new fuels and that commercial airlines will soon go over to the use of 100 octane fuel. It is stated that a thirty percent increase in the pay-load of a plane can be effected by increasing the octane number of the fuel from 87 to 100.

The use of aromatics for aviation engines has not been successful so far due to the fact that the heads of the engines heat up and cannot be kept cool enough for efficient and trouble-free operation. Redesign of the engines will no doubt make it possible to use aromatics or high aromatic blends in the near future. In this particular case, the high octane fuel (benzene - toluene - xylol) became available before engines were designed to use it efficiently. In the case of isopropyl ether and iso-octane, however, the engines existed before the fuel was developed.

DIESEL FUELS

Slow speed conventional type Diesel engines will operate upon fuels of almost every description. The high speed Diesel, however, requires a special fuel for satisfactory operation. This statement is based upon the data discussed at the 1935 annual meeting of the A.P.I. in Los Angeles, California. The tentative classification of Diesel fuels set up in 1934 by the A.S.T.M. has done a lot of good in bringing the Diesel designers closer to the petroleum refiners. The problem of supplying large quantities of high speed Diesel fuel, of the proper quality, is not solved. It develops that the Diesel fuel of the future may be a blend of petroleum refined oils and organic chemicals. Loomis[11] proposes the use of nitroparaffins to eliminate Diesel knock. Others have proposed the use of alcohol blends as well as the use of diacetylene. The future trend in Diesel fuel for high speed engines will probably be in the direction of addition agents for the purpose of shortening the period between ignition and commencement of pressure. It is known that organic chemicals and other substances, which induce gasoline engine detonation have the reverse effect upon Diesel fuels. An example, amyl nitrite (a knock inducer for gasoline) produces smooth running of a Diesel when added to a "rough running" fuel. This line of endeavor appears promising for the organic chemical manufacturer inasmuch as several chemicals are now known which can be made from petroleum as a raw material and they show promise of becoming useful as addition agents to poor grade Diesel fuels.

PLASTICS FROM PETROLEUM

The synthetic resin branch of this industry is experiencing a phenomenal growth. One of the most important chemicals used in the production of cellulose acetate resins is acetic anhydride, the consumption of which in 1936, amounted to over 100,000,000 pounds. Acetic anhydride can be made from propylene as outlined by Brooks (reference cited) through isopropyl aclohol, acetone, ketene to acetic anhydride. The phthalic anhydride resins produced in the States in 1936 were 34,000,000 pounds or over one-third of the total synthetic resins produced.

ARTIFICIAL SILK INDUSTRY

This industry, in the United States, used large quantities of glacial acetic acid, sulphuric acid, acetone, and ammonia, all of which can be produced from petroleum and natural gas. It may be of interest to mention that some petroleum refiners are making all the sulphuric acid required by them as a by-product of refining sulphur bearing petroleum oils. Plants for the manufacture of ammonia from by-product gases from carbon black plants operating on natural gas, are already designed and need only a slight change in market prices to make it profitable to put such plants into operation.

SOLVENTS, THINNERS, ETC.

The petroleum refiner should not overlook the paint, lacquer and plastics industries as a market for such products as toluene, glycol ethers, ethanolamines, etc., all of which can be economically produced from petroleum. One of the principal base stocks for the manufacture of solvent ethers is ethylene oxide which is readily made from ethylene by direct synthesis. Solvents made by hydrogenation known as "high solvency naphthas" are coming into use by leaps and bounds and here, too, the refiner is well fitted to produce such solvents.

HIGH AROMATIC PETROLEUM SOLVENTS

During the past two or three years the demand for solvents and thinners by the varnish and lacquer industries has grown so rapidly it has been difficult for producers of such solvents to standardize the grades required or prepare satisfactory test methods. Previous to this time solvent naphtha, made from petroleum, was more or less paraffinic in nature and had little or no solvent power for present day lacquer base materials. Coal-tar solvents, composed largely of benzene, toluene, and xylene, were the only solvents known as "high solvency naphthas." Lately, such solvents, or solvents having the proper solvent qualities, have been prepared from petroleum. To date three methods of obtaining aromatic solvents from petroleum have been used, i.e. (1) Extraction of aromatics by selective solvents such as sulphur dioxide (Edeleanu process); (2) Pyrolysis of oils or gases followed by polymerization to aromatics; and (3) destructive hydrogenation of petroleum fractions to aromatic like materials. The first method is applicable only to certain selected crude oils, found in various countries such as Dutch East Indies, United States, and Russia, which oils contain appreciable percentages of aromatics. The second method has been described in this paper, and the third has been practiced by the Standard Oil Company of New Jersey. Mention should be made that the Associated Oil Company[12] has been producing aromatic solvents from California crude oil for several years as has the Union Oil Company of California. Both concerns use the Edeleanu process, according to the articles appearing in the literature.

The naphthas produced are represented by the typical analyses shown in table 1.

TABLE 1—TYPICAL HIGH SOLVENCY NAPHTHAS

Figure 3 is indicative of the type of aromatic distillate produced by the Pure Oil process of polymerization for aromatics.

Of the several tests recommended by individual concerns using the solvents, the Kauri butanol test seems to be preferred. Esso Laboratories prefer this

[11] Loomis, U. S. Patent No. 1,820,983.
[12] Lazar, Arthur, Varnish & Lacquer Diluents, *Ind. Eng. Chem.*, Vol. 28, No. 6, June, 1936, p. 658.

TABLE 1
Typical High Solvency Naphthas

CLASS	A	B	C	D	E	F	G
Gravity A.P.I. at 60° F.	47.0	30.1	26.6	46.8	38.2	37.1	31.4
Gravity Spec. at 60° F.	.7927	.8756	.8950	.....	.8338	.....	.8686
Color	+23	+23	+16	+30	+21	+25	+25
Doctor	Negative	Negative	Negative	Negative	Negative	Negative	Negative
Corr. Full Dist. Cu. Strip	Not Passed	Not Passed	Not Passed	Passed	Passed	Passed	Passed
Corr. A.S.T.M. Cu. Strip	Passed	Passed	Passed	Passed	Passed	Passed	Passed
Aniline Cloud Point	55° F.	19.4° F.	16.4° F.	.....	32° F.	44° F.	36° F.
Kauri Butanol Value	59.2 cc	72.8 cc	74.7 cc	.....	66 cc	68 cc	65 cc
Dimethyl Sulfate Value	32.5%	44%	43%	.....	32%	32%	32%
Flash, Tag closed Cup	.....	84° F.	124° F.	.....	84° F.	94° F.	144° F.
Neutrality of Residue	Neutral	Neutral	Neutral	.....	Neutral	.....	Neutral
Color of Residue	Dark Brown	4½-5NPA	4½ NPA	.....	.....	.....	.....
Distillation:							
Initial Boiling Point	183° F.	281° F.	330° F.	204° F.	281° F.	293° F.	365° F.
5%	210	310	364	212	294	301	370
10%	214	317	371	214	298	304	371
20%	218	331	376	216	304	306	372
30%	222	341	380	219	309	309	375
40%	225	353	382	222	313	312	377
50%	229	363	384	225	318	315	379
60%	233	372	386	229	323	318	382
70%	238	380	390	233	330	323	385
80%	244	388	393	238	335	329	389
90%	256	395	398	247	345	338	396
95%	266	400	403	258	570	347	401
Dry End Point	274	407	409	270	579	358	408
A.S.T.M. End Point	281	410	412	280	582	361	415
Recovery	28.5%	98.5%	98.5%	99.0%	98.5%	99.0%	98.5%
Residue	1.0	1.0	1.0	0.3	1.0	0.9	1.0
Loss	0.5	0.5	0.5	0.7	0.5	0.1	0.5

test for hydrogenated solvents and gave as their reasons the following:[13]

1—According to published data and the author's experience, both the Kauri butanol test and the dilution ratio classify solvents in the order of their aromaticity.

2—Specifications for the use of petroleum solvents as lacquer diluents often include minimum Kauri butanol value.

3—The Kauri butanol test is a more sensitive index for indicating change in aromaticity than the dilution ratio. The work of improving the Kauri butanol test is fully reviewed in the quoted article.

These data are included here because the high solvency naphtha demand is growing and the field for varnish and lacquer diluents is one of the most promising for the petroleum refiner.

[13] Baldeschwieler and Troeller, *Ind. Eng. Chem.*, Vol. 7, No. 6, Nov. 15, 1935 (Analytical Edition).

NEW PRODUCTS FOR NEW USES

Space and time are not permitted here to describe

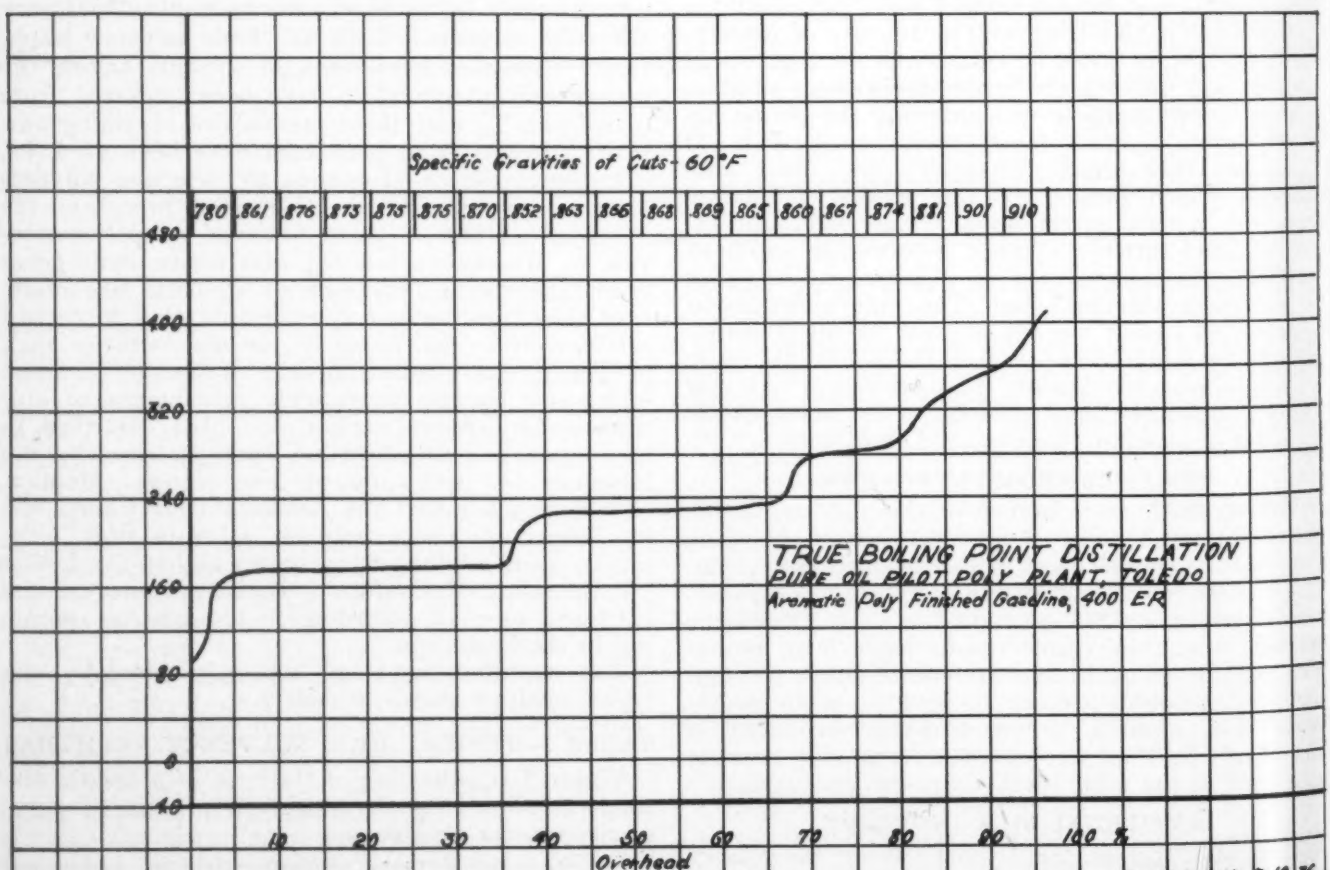

Specific Gravities of Cuts - 60°F
.780 .861 .876 .873 .875 .875 .870 .852 .863 .866 .868 .869 .865 .860 .867 .874 .881 .901 .910
480
400
320
240
160
80
0
40
10 20 30 40 50 60 70 80 90 100 %
Overhead
TRUE BOILING POINT DISTILLATION
PURE OIL PILOT POLY PLANT, TOLEDO
Aromatic Poly Finished Gasoline, 400 ER
Dunkirk N.Y. 5-19-36

FIGURE 3

the various chemicals which are already being made from petroleum. Research and development now going on will no doubt give rise to a host of new organic chemical compounds from petroleum and natural gas.

In turning from organic chemicals used in our daily routine, to those chemicals to be used in the national defense we know that combat gases of deadly effectiveness can be made from petroleum and natural gas. It is now apparent to informed technologists that any nation which has a supply of hydrocarbon gases or liquids can produce huge quantitites of mustard gas, diphosgene, hydrocyanic acid, and other weapons. It is to be hoped that the occasion for their use will not arise in the future.

Synthetic rubber is now being made from petroleum and this fact makes it possible for this necessary war material to be produced within the borders of almost any nation.

Emphasis is now being placed on the use of catalysts as the most promising route to follow for the synthesis of organic chemicals from petroleum. Many new and astounding announcements can be expected along this line as time goes on. No one can predict the products to be made from these raw materials.

It is not clear at the moment just what effect the new art of organic chemical manufacture from petroleum and natural gas will have upon the fermentation alcohol and coal tar industries. Economics will be the determining factor in most cases but with the present unbalanced international trade the replacement of alcohol and coal tar as raw material is uncertain. The same is true of the sulphur market. It is well known that high sulphur crude oils have been shunned in late years by the refiners because of the difficulties of refining them for removal of sulphur. With the perfection of the Chemico Process for producing water white sulphuric acid from sulphur gases and sulphur sludges from petroleum, a new supply of sulphur has been found. As petroleum becomes harder to find and its uses increase it is reasonable to assume that the sulphur mining industry is vulnerable as soon as the low grade, high sulphur crude oils and sulphur bearing natural gases increase in use. Several large deposits of crude oil containing 3 percent sulphur are being held for better market prices. When it is realized that more than 150,000,000 tons of crude oil was used in the United States last year and that its replacement by two or three percent sulphur crude oil would make available 3,000,000 to 4,500,000 tons of sulphur a year, then it is apparent that all of the sulphuric acid made last year could be produced without using any mined sulphur. The 1936 production of sulphuric acid was reported as 6,750,000 tons (50 Be').

SUMMARY AND CONCLUSIONS

1—It is believed the pyrolysis-polymerization process will become a major refinery operation rather than play the role of an accessory process.

2—A new organic chemical industry, based upon petroleum and natural gas as raw materials, is now forming and will grow very fast during the next few years.

3—Research trends appear to be in the direction of catalytic processes.

4—The fermentation alcohol and coal-tar industries will probably be affected most by the new industry.

5—The refiner is destined to become an organic chemical manufacturer instead of remaining solely a producer of gasoline and lubricants.

6—As petroleum becomes harder to locate and its products become more expensive, coal and shale oil will some into use as raw materials for organic chemicals, fuels and lubricants. There seems to be some question about agriculture regaining the fermentation alcohol field and if it does not, soil conservation to a higher degree, will take place.

Flanged Joints

[*Continued from page 423*]

From Tables 5 and 6, it may be seen that the contact-pressure ratio, which is probably obtained in bolted up flanged joints, is in most cases much higher than the generally recommended figure of approximately 9.0. If it is true that a gasket contact-pressure ratio of 9.0 indicates a satisfactory joint that will not leak, then the reason for the apparent success of the standard flanged joints may readily be seen. However, the values in Table 5 show a variation of from 36.0 to 13.2 and those in Table 6 show a variation of from 36.3 to 8.0. This still indicates that the different sizes of joints are not so designed to be equally effective in service.

The sizes in which the flanged joints show particularly low values for the contact-pressure ratio are liable to develop leaks while in service. Strains resulting from the manner of installing piping may affect the flanged joints. If the bolts are considered as being elastic members in the flanged joint assembly, any forces set up in the piping acting in such a direction as to separate the flanges, will reduce the contact-pressure ratio on the gasket. These forces may cause sufficient reduction of gasket pressure that leakage at the joint will occur.

From the available information, flanged joints in the 150- and 300-pound standard classifications, with the generally used raised facings, show a wide range of variation when investigated from a design standpoint. Some sizes are more subject to leakage than others when placed in service. Consequently, it is necessary that more careful attention be given to the erection of certain sizes of piping systems than may be required by other sizes. On some sizes unusual care must be taken to prevent leaks and on others over stressing of the bolts is likely to occur. By cautious erection, the standard joints may be successfully used but should it seem desirable that better proportioned flanged joints be used for a particular installation, it is necessary to utilize special facings on the flanges.

REFERENCE

[1]Piping Handbook, Walker & Crocker.

TABLE 6

Pipe Size, Inches	Contact-Pressure Ratio	Pipe Size, Inches	Contact-Pressure Ratio
2	35.7	10	14.8
2½	36.3	12	12.3
3	23.9	14	14.3
3½	21.0	16	12.3
4	16.5	18	10.5
5	12.4	20	9.0
6	14.8	24	8.0
8	12.3	..	...

Special Products Plant Enlarged and Improved

J. C. ALBRIGHT

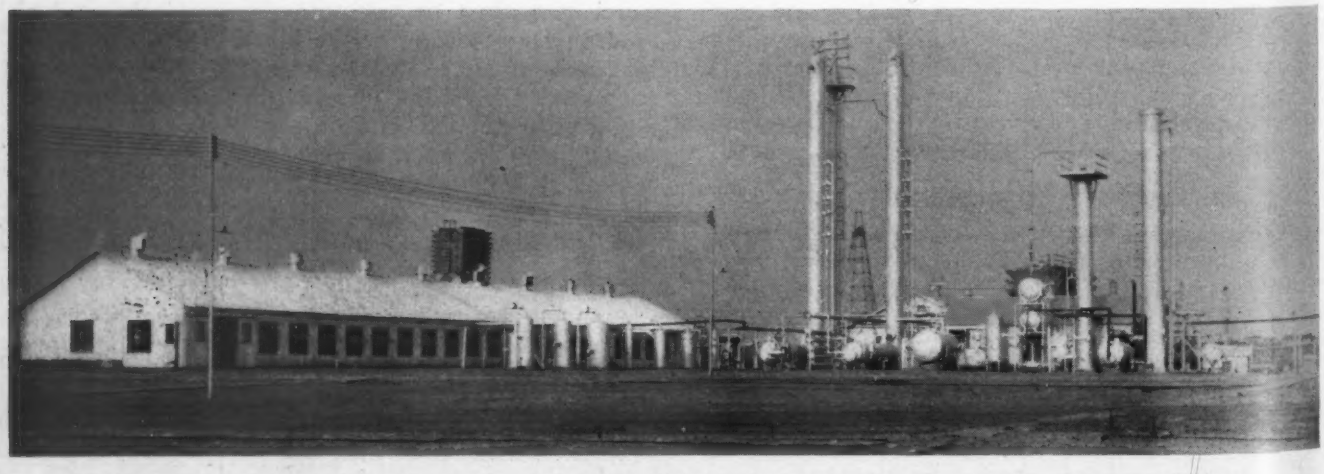
SKELLY OIL COMPANY recently completed building and modernizing several plants in Osage County, Oklahoma. Gasoline produced from them is transported by pipe line to a special products plant at Lyman to fractionate several cuts out of the raw material, including propane and butane. The plant at Lyman has been used as a special products plant for a number of years, manufacturing "Skelgas," butanes and a number of close-cut, narrow boiling-range gasolines for thinners, rubber solvents and the like, even going so far as to place on the market petroleum products meeting specifications of the United States Pharmacopoeia.

Recently, to meet more rigid specifications, and to enable the plant to manufacture these products in larger quantities with less supervision and laboratory control, the company installed three new columns; one for propane, another for butane, and the third to dehydrate the propane by forcing a super-saturation of the moisture in the ethane removed from the propane. As the plant is now being operated, as much as 75,000 gallons of raw natural gasoline may be processed daily, with three principal products being obtained. In normal operation of the plant as a part, excluding the special products column, propane, butane and pentanes and heavier are regularly turned out by the three columns in the plant proper.

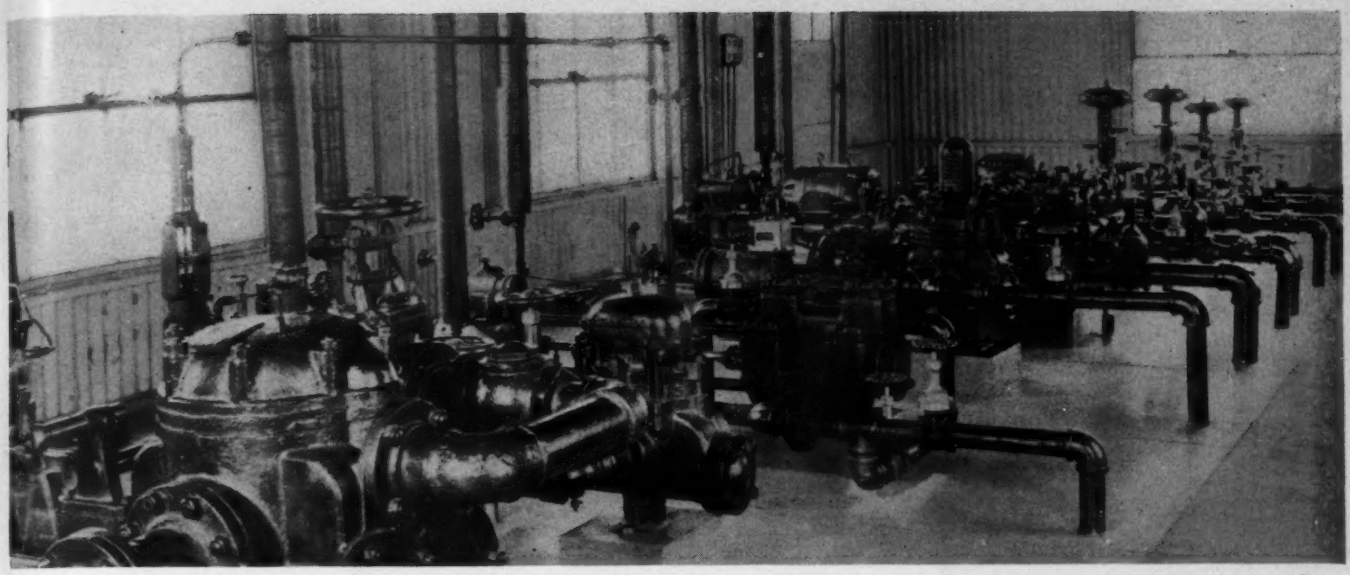
Previous to modernization, other plants in Osage County, several miles to the southeast, were operated as individual units, producing all grades of natural gasoline as well as propane and butane. None of these plants are being operated as fractionating units, but equipment remains in place for processing, should conditions demand that local gasoline be handled in that manner instead of being pipe lined to the special products plant at Lyman.

All gasoline is received in the working storage battery at Lyman without treatment of any kind, containing all the propane possible without the inclusion of excessive amounts of ethane. Reciprocating pumps are used on the pipe line, stations being maintained at each plant to handle individual production. After being gauged into storage at Lyman, the raw, unstabilized gasoline is pumped directly to the first tower in the plant proper. This tower, as well as the next succeeding one used for butane extraction, is 3½ feet in diameter and 60 feet in height. Both have identical reboilers, and similar control equipment.

The propane, or first column receiving the gasoline, is operated at about 320 pounds pressure, with the raw material passing through the usual heat exchanger, counter-current to the bottoms, which are propane free. The exact operation of the column varies somewhat, depending upon the composition of the charge, and the closeness of the overhead cut desired. When propane alone is being manufactured as a product coming from the top of the column, this material is condensed in atmospheric-type coolers placed in the usual type of cooling tower. Reflux ratios vary, of course, but are maintained to produce



Results of modernization of gasoline plant when Skelly converted its Lyman unit from the usual gasoline operation to special fractionation to handle production from all plants in Osage County. Columns on left are new butane and propane with propane dryer back of left column.



Pumps used by Skelly Oil Company in its special products plant at Lyman.

a uniformly pure product in the overhead vapor line.

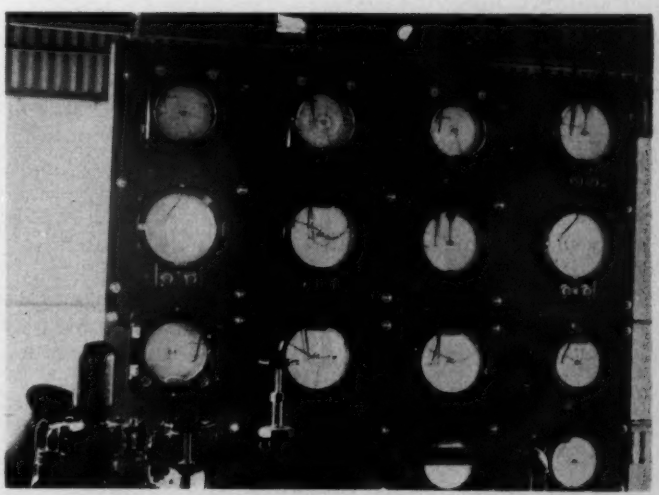
The bottoms from the first column are transferred immediately and constantly to the next column for extracting the butane from the residue. Condensed propane is pumped after cooling and condensing to the dehydrator, which is a column 3 feet in diameter and 55 feet high. This tower was built for a working pressure of 750 pounds, but conditions of dehydration do not require pressures much above 400 pounds. The results obtained in dehydrating the propane depends largely upon the condition of the raw natural before it is pumped to the propane column. Methods are followed in this plant and others which furnish the raw gasoline, to eliminate as much as possible of the moisture before it is placed in the plant working tanks. Settling, due to time, and bleeding the tanks often, is followed consistently so that no free water will enter the working storage before processing the gasoline.

Temperatures applied to the propane in the reboiler of the dehydrating column are controlled at the inlet of the steam to the shell. Temperatures on the overhead connection where the ethane and moisture leave the column are controlled by instruments placed in the water condenser feed line. Reflux on this column is obtained by direct condensation from sections installed on the top of the tower, maintaining a sufficiently low temperature that all propane is driven back down the column to the base outlet. Dehydrated and de-ethanized propane from the base of this column is removed by remote controlled liquid valves with an instrument on the side of the reboiler which regulates the level in the column.

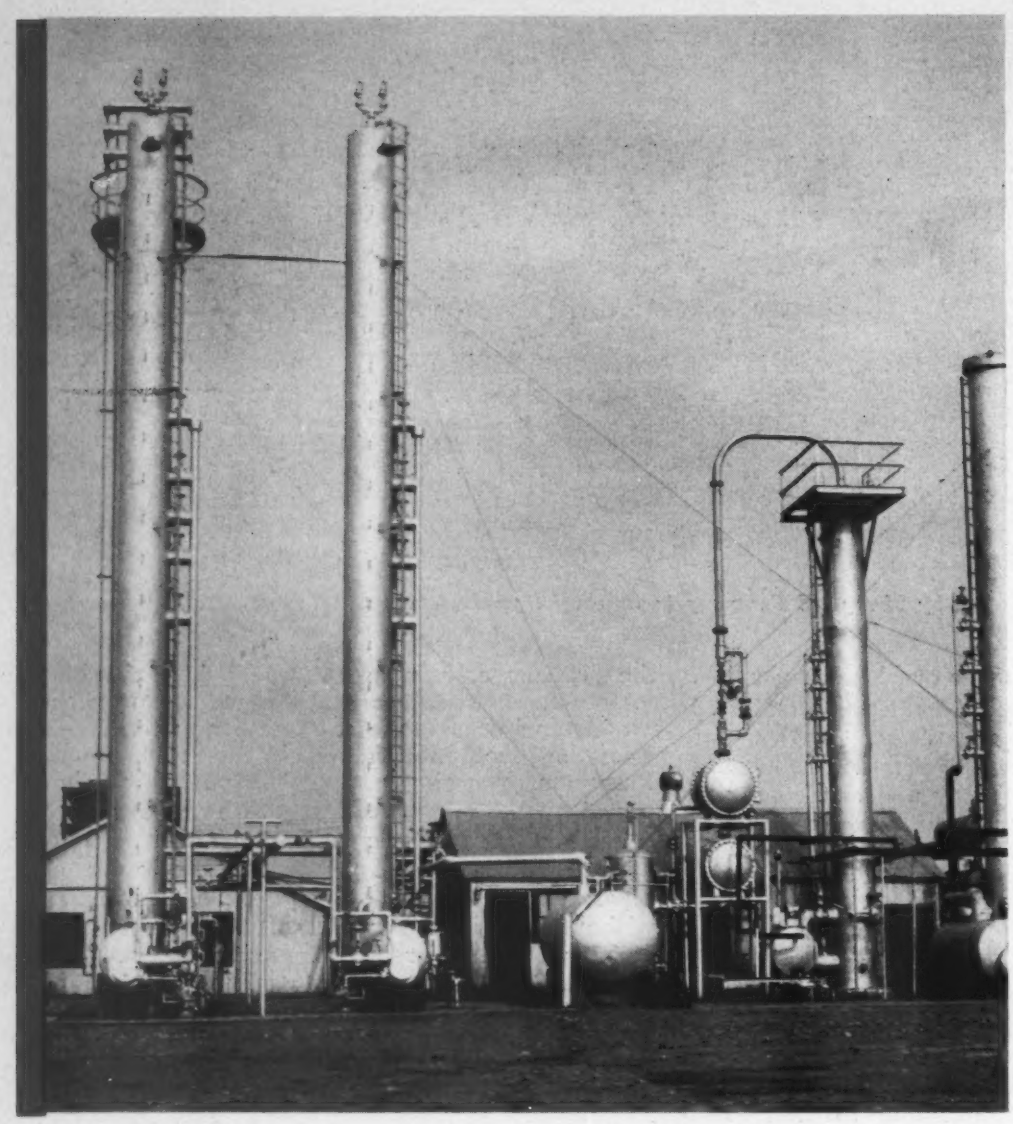
Finished propane is transferred to working storage at the plant, after which it is pumped to bottle filling racks, or tank cars on the siding nearby for shipment in bulk. A large part of this production formerly was bottled exclusively and shipped in this manner, but since tank cars have been designed which will transport high vapor pressure liquefied petroleum gases, bottling has gradually declined at Lyman in preference to bulk shipments.

Butane and heavier products in the gasoline from the propane column are transferred to the butane column for extraction of the butane as an overhead product, while pentane and heavier material passes from the base of the column in the regular manner. Pressures averaging around 150 pounds are maintained on the second column, with the butane condensed in atmospheric sections. Reflux ratios are maintained in this tower that will provide close separation of the butane from the heavier material without carrying over any of the heavier hydrocarbons. Like the propane, butane is shipped largely in tank cars. A large part of the production is shipped to industrial centers to be used in different processes which call for heats easily obtained by using butane for fuel.

The butane column is operated almost continually in separating the butane from the heavier material, but occasionally the butane and heavier are processed in the column to manufacture any grade of natural gasoline up to 26/70. However, it has been the practice to separate all the butanes from the remainder of the gasoline in continuous operation, storing the butane in pressure vessels and later



Plant operations are controlled through this instrument board.



Two identical columns on left supersedes columns on right for manufacture of propane and butane in Skelly's Lyman gasoline plant in Osage County, Oklahoma.

blending back with the butane-free gasoline in sufficient quantities to make any grade of gasoline from butane-free up to 26/70.

The bottoms from the butane tower are released through liquid-level controls to working storage at the special products columns where it is again processed through two columns to make any grade of material desired. Pure hydrocarbons or combinations of several may be cut from the columns in the specialty plant to meet requirements of purchasers, but occasionally shipments are made which include portions of several cuts which are made by blending one with another before loading out.

No operation in this plant or any of its processes is carried out by manual control. Instrumentation has been carried out here to include all operations from regulation of circulated water to volumes of liquids charged to the columns. In some instances, instrument-controlled valves are installed directly in the line, for example, the water to the top of the propane dehydrating column for cooling the reflux, passes through the by-pass, which is partially closed with a gate valve, but the controlling amount flows through the main line past the instrument-operated valve. Steam to the reboiler is controlled by the by-pass, with the main line opened sufficiently to admit the normal volume of heat. Instruments which control the speed of the pumps, the amount of water to the overhead condenser and various other operations are all concentrated in the pump room and mounted upon a panel for convenience in servicing and reading.

Ordinarily, the propane and butane manufactured from natural gasoline produced in Osage County are sweet and non-corrosive, not requiring treatment of any kind before shipment. Heavier materials are usually treated unfractionated with concentrated hypochlorite to remove objectionable compounds which may be in the liquid. After treating, the butane-free gasoline is handled in the specialty columns, which are also highly instrumentized. A large part of circulating the liquids, especially reflux and some of the special products, is obtained through this part of the Lyman plant with turbine type, electric-driven pumps running at constant speed.